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Evaluation of the General Motors' Double Alkali SO2 Control System

Arthur D. Little, Inc, Cambridge, Mass

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16. ABSTRACT The report is an evaluation of the double alkali flue gas desulfurization (FGD) system, installed to control SOx emissions from the coal-fired industrial boiler complex at General Motors' Chevrolet plant in Parma, Ohio. It describes the boiler and FGD systems. It addresses performance with respect to SO2 removal, filter cake properties, lime stoichiometry, carbonate softening, soda ash stoichiometry, scaling, oxidation, and reliability. The evaluation is presented in terms of three 1-month-long intensive test periods and a longer-term non-intensive test period. System material balances are presented for some of these periods. A general history of the operation is also presented.

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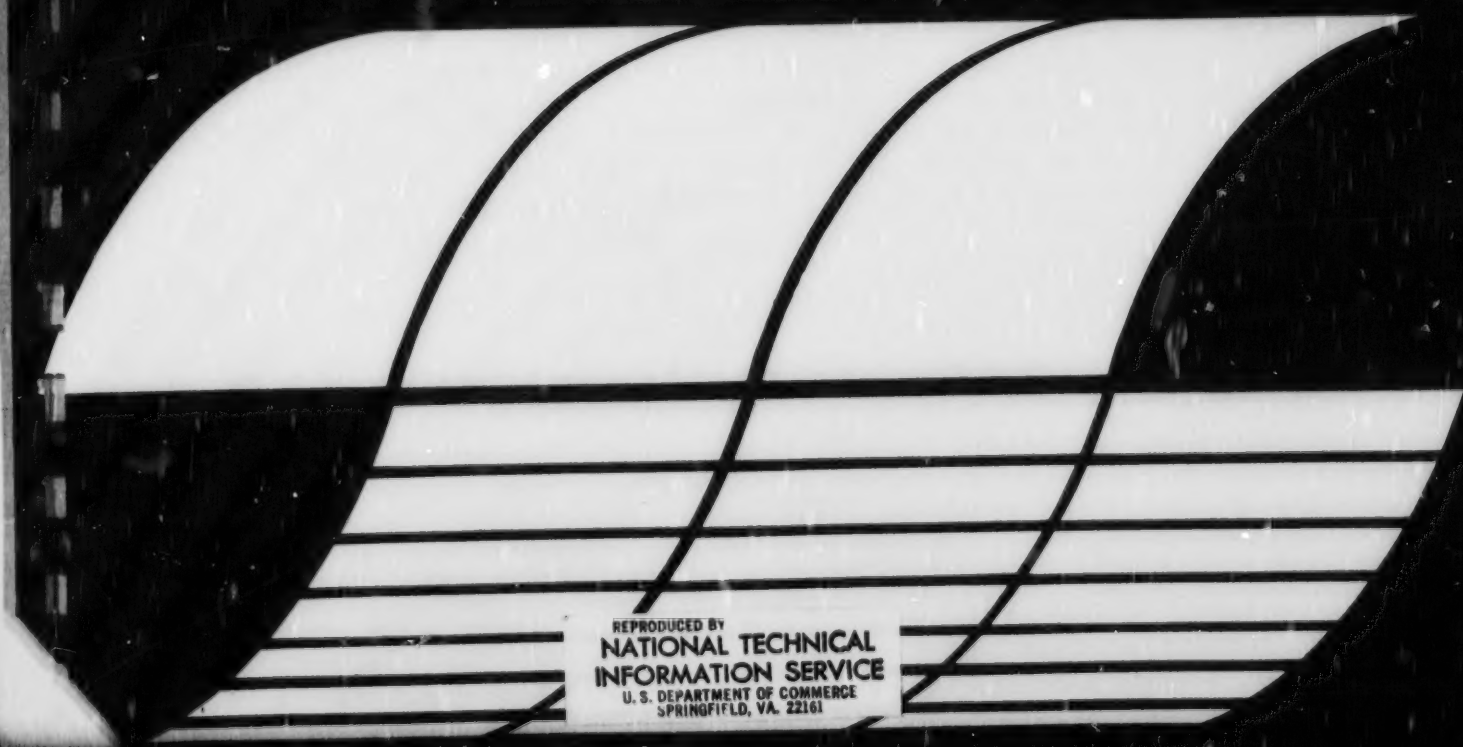

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EVALUATION OF THE GENERAL MOTORS' DOUBLE ALKALI SO_2 CONTROL SYSTEM

by

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I. SUMMARY

The purpose of this test program was to obtain data to characterize the GM system from the standpoint of SO_2 removal, process reliability, sulfate control, waste characteristics, degree of closed loop operation (i.e., sodium makeup versus losses), lime and other chemicals utilization, and material balances on the overall system and the important component parts. Both GM and ADL had responsibilities for data acquisition, while ADL, under contracts to GM and EPA, performed the chemical analyses. The program consisted of three one-month intensive tests and 18 months of lower level non-intensive testing, including six months of formalized process data acquisition.

During the test program which covered the period August 19, 1974, to May 14, 1976, the General Motors Double Alkali system at Chevrolet-Parma, Ohio, showed significant improvement in both process and mechanical performance. A number of operating modes were investigated by GM in accomplishing this improvement. The mode of the final intensive test, April 17, 1976, to May 14, 1976, showed the greatest promise for a viable long term operation.

A. Results and Conclusions

The important results of the test program are summarized in Table 1. The key results excluding SO_2 removal are based on the average cake compositions over each entire run and therefore are the best indication of the actual performance for the extended periods.

1. SO_2 Removal

Despite the low SO_2 concentration in the flue gas of 800-1300 ppm (vol.) caused by the high excess air used by the boilers, the SO_2 removals have been excellent, in the range of 90%. This is well above the average statutory requirement of about 60-70% for the coals burned (1.5-3.3% S, 11,000-13,500 Btu/lb). In one experimental operating mode, which has now been abandoned, the average removals fell to the 65% range.

2. Filter Cake Properties

The filter cake properties as measured by percent total solids (56% solids) and solubles content (0.03 mole Na_2/mole SO_x in cake) improved dramatically in recent operation. Waste properties were better than target levels for dryness (minimum of 50% solids) and for cake wash efficiency (solubles recovery equivalent to a maximum loss of 0.05 mole Na_2/mole SO_x in the cake). The drier solids have resulted in a lower sludge hauling requirement while the decreased solubles loss improves the environmental acceptability of the cake for disposal. It should be noted that although cake washing to a low solubles loss rate has been demonstrated, this rate does not correspond to the expected long term soda ash stoichiometry of 0.05 mole Na_2/mole SO_x. At steady state, the sodium content of the cake must match the carbonate (as soda ash) used for softening the regenerated liquor, as further discussed in Section 6. Soda Ash Stoichiometry.

Table 1

KEY OPERATING PARAMETERS AND RESULTS

Operating Period	8/19/74-9/13/74	2/17/75-3/14/75	4/19/76-5/14/76
SO_2 Removal	90-95%(rpt. by GM)	65%	90%
Recycle pH	5.5-6	7-7.5	6.0
Scrubber Feed Location	Top Tray	Recycle Tank	Recycle Line
Lime Stoichiometry mole Ca/mole S in cake	1.90	1.65	1.32
Soda Ash Stoichiometry mole Na_2/mole SO_x removed	--(2)	0.08	0.12
Solubles Loss mole Na_2/mole S in cake	0.11	0.12	0.03
Oxidation mole $CaSO_4$/mole $CaSO_x$ in cake	60%	47%	83%
Ca++ in Scrubber, ppm	305	465	490
Scaling?	Yes($CaCO_3$)	Yes($CaSO_3$)	No
Na+ = Total, M in Scrubber Feed	0.58	0.66	0.96(1)
Na+ - Active, M in Scrubber Feed	0.087	0.13	0.12
Cake Washing?	No	No	Yes
Total Solids, wt.%	47.1	41.4	56.0
Soluble Solids, wt.% of Wet Solids	2.4	2.4	1.0
Insoluble Solids, wt.% of Wet Solids	44.7	39.0	55.0
Soluble Solids/Total Solids	0.05	0.06	0.02

(1) Includes ~0.18M Na+ as NaCl

(2) No data taken on SO_2 removal

3. Solids Dewatering

The ease of solids dewatering (settling and filtration) also improved dramatically as mirrored by the improvement in cake dryness discussed above. Elimination of underflow recycle to the clarifier center wells and the reactor system lowered the gross load on the clarifier and solved the temporary problems of solids overflow and poor solids concentration. Increased total oxidation (from 50-60% to 83%) by air sparging in the scrubber bleed lines was significant in improving the solids filterability as measured by dryness.

4. Lime Stoichiometry

The lime stoichiometry improved consistently over the test program from 1.90 to 1.32 mole Ca/mole SO_x in the final test period. This improvement reflects: better control of lime feed; the use of hydroxide concentration to monitor and control excess lime fed; and the increased concentration of sodium ion in the liquor which permits hydroxide solubility to reach the target level of about 0.1M. Although the lime usage is still somewhat high, we expect that with continued close control, the stoichiometry can be appreciably further reduced. The minimum level will be limited only by reactor residence time which is about one hour when two scrubbers are operated.

5. Carbonate Softening

Two methods were used for softening of the regenerated liquor: sparging of gaseous carbon dioxide into the liquor; and addition of soda ash feed in the center well of the softening clarifier. Both methods are effective in reducing the soluble calcium from saturation to levels of concentration below 400 ppm. However, carbon dioxide forms an acid in solution neutralizing two moles of hydroxide per mole of calcium precipitated and making the job of SO_2 removal more difficult in the scrubber. Further, lime stoichiometry must increase in order to provide the additional hydroxide. Other drawbacks of CO_2 softening are the relatively poor-settling calcium carbonate it produces and the filter cloth blinding by the finely divided $CaCO_3$. Therefore, soda ash softening, to the extent that long term sodium balance can be achieved, is the only viable approach.

6. Soda Ash Stoichiometry

Soda ash is fed to the system for two purposes: (1) to provide sodium ion to replace that lost in the cake and (2) to provide carbonate ion to precipitate soluble calcium from the regenerated liquor. With adequate cake washing, the softening requirements set the minimum soda ash addition rate.

During the early months of operation when the filter cake was not washed, the sodium loss was above 0.1 mole Na_2/mole SO_x in the cake. After cake washing was initiated, the loss was reduced to as low as 0.028 mole Na_2/mole SO_x for an extended one-month average.

At this low sodium loss rate soda ash must be added to the system in the same proportion of SO_2 removal, i.e., 0.028 mole Na_2CO_3/mole SO_2 removed. If more were added, there would be an accumulation of Na_2SO_x in the system over time.

This quantity of carbonate addition is sufficient only to reduce the soluble calcium in the regenerated liquor about 85 ppm from the saturation level of about 800 ppm. Without having attempted a demonstration at such a low softening level, General Motors estimates that a soluble calcium reduction of 150 ppm (to 650 ppm total) can be a viable operational approach. This corresponds to a soda ash makeup rate of 0.05 mole/mole SO_2 removed which would subsequently appear in the cake as a soluble sodium loss of 0.05 mole Na_2/mole SO_x in the cake.

7. Scaling in Scrubber Loop

There have been two sets of circumstances leading to solids deposition in the scrubber loop. The first was carbonate scaling on the top tray due to poor liquid mixing on the tray with resulting localized high pH and carbonate scrubbing. This problem has been eliminated by effective mixing of the high pH regenerated liquor with the more acid recycle liquor before entering the top tray.

The second was calcium sulfite plugging which resulted from a combination of factors in an experimental operating mode, since abandoned.

Throughout the test program, including the above situations of solids precipitation as well as the problem-free periods, the soluble calcium level in the scrubber loop has been in the range of 350-550 ppm. This compares with a saturation level of about 800 ppm. The problems have been solved and no such scaling has occurred in the last 12 months. Importantly, the degree of softening (soluble calcium reduction) usually performed has resulted in a calcium ion concentration reduction of 250-450 ppm below saturation level. Since there has been no extended operation below this range, it is not clear how little softening can be performed before encountering calcium sulfite or other scaling problems, although some reduction can probably be tolerated. GM estimates that operation at a soluble calcium level of about 650 ppm would be viable.

8. Oxidation

The oxidation rate in the scrubbers has been about 45-60% of the SO_2 removal rate, owing to the high excess air in the boilers and the resultant high oxygen content of the flue gas relative to the SO_2 concentration. Further oxidation to improve solids properties was attempted in two ways: (1) by sparging air into chemical mix tank #1 while solids were recycled or while lime was added to the same vessel; and (2) by sparging air into the scrubber bleed liquor upstream of the chemical mix tank. The latter was the only effective method, increasing oxidation beyond that in the scrubbers by about 30% of the total SO_2 removal.

The system has demonstrated its capability of removing (precipitating) sulfate at even the highest oxidation rates, i.e., greater than 90%.

9. Entrainment

Liquor and soluble solids entrainment in the scrubbers has occurred periodically. In a test authorized by GM, an average of about 0.019 m^3/hr (5 gal/hr) per scrubber was found to be entrained in the treated flue gas. Although somewhat high, this was within the design specification.

Assuming an average scrubber liquor containing 0.5M Na_2SO_4, we project that about 1.4 kg/hr of soluble solids entrainment at the full capacity of a single scrubber.

10. Reliability and General Status

The system was developmental throughout the test program and as such did not generally perform in accordance with design criteria. It did, however, show substantial improvement over time.

Because of the continuing developmental nature of the system, many of the outages, particularly the longer ones, were for mechanical modifications to accommodate new modes of operation. In all, the total scrubber availability to the boilers over the test program was 77.9% excluding four long-term planned shutdowns for system modifications. Therefore, the General Motors Double Alkali Process has not yet been proven over an extended period to be a commercially viable process for SO_2 control. Because of recent process improvements demonstrated in the four-week test in April-May 1976, we believe the system is now capable of proving its long term reliability.

The expected long term operating parameters for the General Motors Double Alkali system are summarized in Table 2. These are based on demonstrated operation as well as projected steady state criteria.

C. Recommendations

1. System Operation

a. General Motors should continue to operate the plant in much the same mode that proved successful during April-May 1976.

b. GM should commit to an extended demonstration of system reliability to show that the plant is capable of operating at these optimal levels for long periods of time with a high availability factor. A test of 6-12 months is desirable during which operating hours, SO_2 removals, chemical makeup rates (based on feeds and apparent stoichiometries from cake), and filter cake properties would be monitored regularly. In the early stages of this reliability demonstration, particular attention should be given to reducing

Table 2

PROJECTED OPERATING PARAMETERS

GENERAL MOTORS DOUBLE ALKALI SYSTEM

SO_2 removal	90%
Softening, reduction of Ca++	150 ppm
Soda ash addition, as Na_2	0.05 mole/mole SO_x removed
Solubles loss, as Na_2SO_4	0.05 mole/mole SO_x in cake
Lime stoichiometry	<1.3 mole/mole SO_x removed
Solids properties	
dry solids	55%
solubles as Na_2SO_4 (wet basis)	2.8%

excess lime feed, based on a reactor pH of about 12, and to closing the material balance on sodium. Later, as it becomes possible, further oxidation of the bleed liquor should be attempted to determine if further improvement of cake dryness is feasible.

2. Double Alkali Process Technology

Double alkali technology should continue to be pursued as a viable option for industrial boiler SO_2 control.

In the operation of its system, General Motors has acquired considerable practical knowledge of both the process variables and, particularly, of the mechanical considerations involved in such a system. This knowledge should be used as a valuable resource by those contemplating the implementation of double alkali process technology.

II. INTRODUCTION

A. Background

In March 1974, General Motors started up its demonstration SO_2 control system at the Chevrolet Parma (Ohio) Plant using a double alkali wet scrubbing technique developed in their prior pilot work at the same facility.

The steam plant at the Parma facility contains four boilers, two with a nominal steaming capacity, two at 27,300 kg/hr (60,000 lb/hr) and two at 45,500 kg/hr (100,000 lb/hr). They are spreader stoker-fired with traveling grates and operate with variable excess air rates in the 100% range. Normally burning high sulfur (2-3%) eastern coal plus occasional lower sulfur waste oil, the raw flue gas generally contains 800-1300 ppm volume of SO_2. The two larger boilers are equipped with economizers with resultant lower flue gas temperatures than the smaller boilers. There already were existing mechanical dust collectors on each boiler for primary particulate control.

Each scrubber was installed to control the emissions only from its respective boiler, i.e., no provision was made for crossing over from one scrubber to a parallel one while operating the same boiler. Booster fans were installed upstream of the scrubbers where the flue gas is dry.

Since the scrubbers were required to provide only a modest reduction in particulate loading from 0.73 to 0.12 gm/Nm^3 dry (0.3 to 0.05 gr/scfd), they were to be principally SO_2 removal devices. As such, they were designed as three-tray columns (not high energy scrubbers such as venturis) with quench spray sections at the inlets and unwashed, full-diameter wire mesh demister pads at the outlets. Provision was made for indirect reheat of the flue gas using 175 psig steam to heat a fresh air stream which is then mixed with the treated flue gas.

Figure 1 is a generalized flow schematic of the General Motors system (Figures 4-7 in Chapter III show the specific schemes employed during the test program). In the scrubber, SO_2 removal is effected by contact, at an L/G of about 2.7 ℓ/m^3 (20 gal/1000 cu. ft.) of saturated flue gas, and reaction with a circulating sodium solution by the following reaction sequence:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

Simultaneously, some of the oxygen present in the flue gas participates in the oxidation reaction

$$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4.$$

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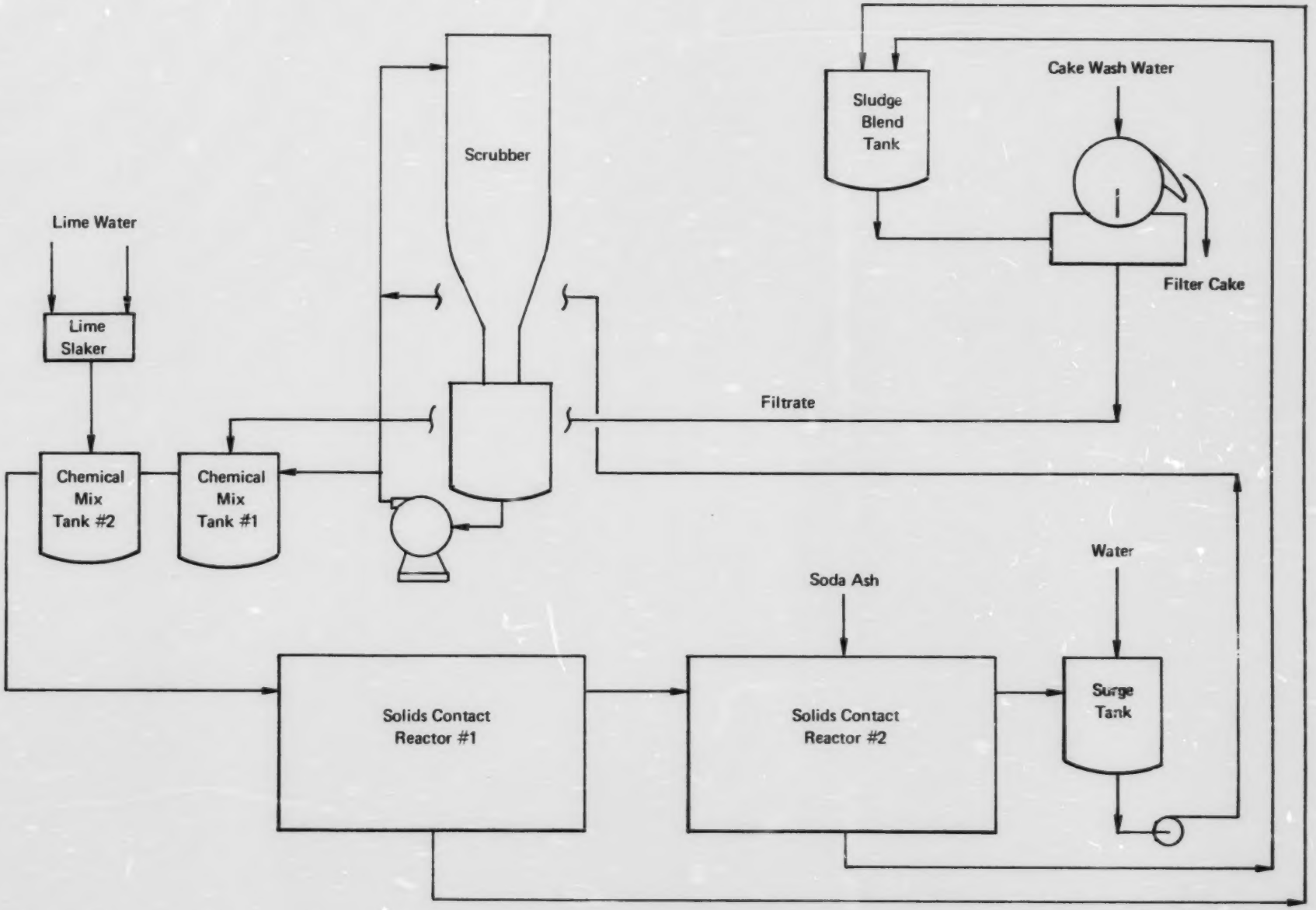

FIGURE 1 FLOW DIAGRAM – GENERAL MOTORS DOUBLE ALKALI SYSTEM

A portion of the circulating liquor containing a mixture principally of sodium sulfite, sodium bisulfite and sodium sulfate is bled to a reactor/clarifier system where the sodium value is regenerated for recycle to the scrubber by reacting the solution with lime:

$$2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3\downarrow + 2H_2O$$

$$Na_2SO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_3\downarrow$$

$$Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4\downarrow$$

A residence time in the lime reactor of five minutes was provided at full design flow. In practice, however, it has been more nearly 30-60 minutes at the lower operating rates and sometimes using two reactors (chemical mix tanks).

After the precipitated solids are further reacted and concentrated in a 18.3 m diameter, 4.3 m high clarifier, the liquor is softened in a second equal-size clarifier to minimize the opportunity for deposition of calcium salts in the scrubber. The clarifiers provide for a surface rise rate of 1.1 m/hr (0.46 gpm/ft^2) at the design flow rate. Slurry is withdrawn as underflow at about 15-20% solids.

Softening is accomplished by reaction with fresh soda ash feed which serves also to replenish sodium to the system.

$$Ca^{++} + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2Na^+$$

Alternatively, if soda ash is not required to the full extent of softening, carbon dioxide may be added also.

$$Ca^{++} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+$$

However, since this has the effect of increasing the lime requirements to maintain the regenerated liquor pH at a constant value, it is the less preferred softening route.

The slurry underflows from both clarifiers are bled to a surge tank for subsequent rotary vacuum filtration with the filtrate recirculated to the regeneration system and the filter cake sent to disposal. There are two full-size filters installed, each with 46.5 square meters (500 square feet) of cloth area. It was found that nylon cloth afforded better cake release than the originally installed polypropylene although it was less durable.

B. Test Program

1. Plan and Execution

The EPA test program of the GM system as planned and performed by ADL was scheduled to be one year long and was to consist of three one-month intensive

test periods and nine months of non-intensive testing. In the intensive tests the system was to be monitored closely with ADL representatives present and with samples of important process streams withdrawn daily for analysis. In the remaining non-intensive periods, this close day-to-day observation would not be required and frequency of sampling would be reduced to weekly. Field support for the program was to be supplied by ADL to coordinate and supervise the test program, and to observe the system operation, and was to be supplied by GM to log operating data, to withdraw samples and to analyze samples. (Before the start of the test program, manpower availability changed at GM and the analytical work was contracted to ADL by GM for the first intensive test and by EPA for the remainder of the program. GM retained responsibility for system operation, logging of operating data, flue gas analyses and withdrawing of necessary samples.)

In program execution, the test periods were scheduled according to system availability to ensure sufficient data for analysis. As a result, the program was stretched to 2½ months during which three one-month periods of intensive testing and six months of formalized non-intensive testing were performed. The remaining 12 months consisted of a lower level of effort to keep informed of the operation and modifications to the process.

The first intensive test was viewed as a period of orientation to be used to plan the remaining tests. As such, the planned data acquisition was modest requiring no routine gas sampling or sludge weighing. In the second test, data acquisition was more complete. We hoped to observe three scrubbers operating at peak winter loads, but unexpected calcium sulfite plugging in the scrubbers restricted SO_2 removal and ultimately scrubber operability. An average of only one scrubber was run for the month. The third intensive test, in which data acquisition was again relatively complete, went smoothly with two boilers and two scrubbers operated for most of the time.

2. Data Acquisition

Figure 2 shows a generalized flow schematic of the GM plant indicating the sampling and measuring points used in monitoring the process operation. Much of the data was reduced to the material balances described in Appendix B.

3. Analytical Procedures

During the test program a large number of liquid, solid and slurry samples were withdrawn from the system for determination of the relative quantities of liquid and solid present and for analyses of the chemical species of interest. Appendix C describes in detail the step-wise procedures used in performing these chemical analyses.

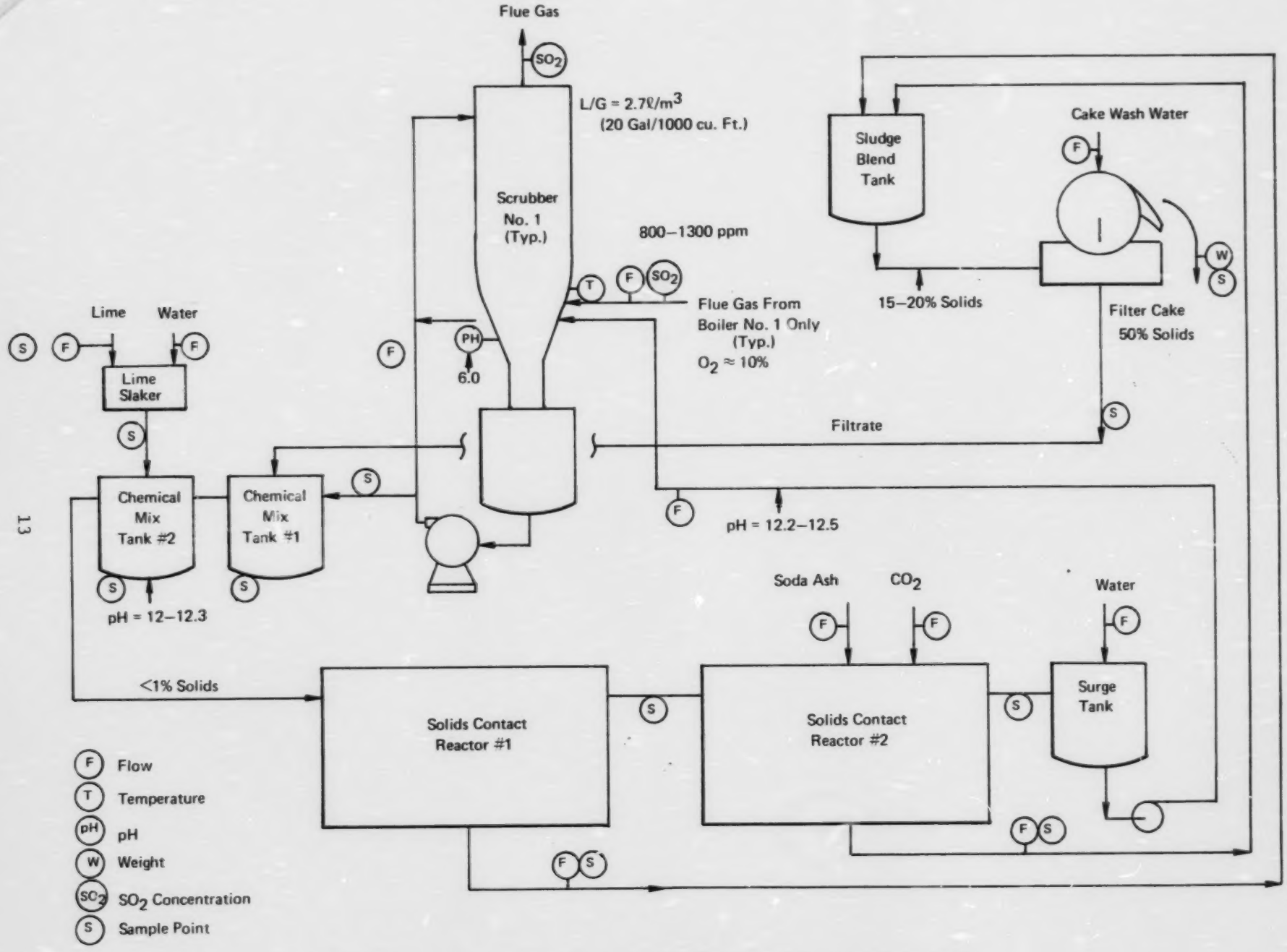

FIGURE 2 DATA COLLECTION POINTS AND NORMAL OPERATING CONDITIONS

III. SYSTEM OPERATING HISTORY

This chapter presents a brief history of the operation of the General Motors Double Alkali SO_2 Control System at Parma, Ohio, from August 19, 1974 to May 14, 1976.

Appendix A shows graphically when the four boilers were in operation and also when the corresponding scrubbers were on. Comments indicating process and mechanical operating difficulties, equipment modifications and the timing of tests are noted on the appropriate dates. Discussion of the important process parameters pertaining to these operating difficulties is included in Chapter IV.

A summary of scrubber availability by month is presented in Figure 3. Superimposed on the total operating hours for each boiler are the hours in which the scrubber actually ran and additionally the percent of hours in which the scrubber was ready but not run. From August 19, 1974, to May 14, 1976, the scrubbers ran a total of 37.5% of the boiler operating hours and were available for an additional 23.5%. The maximum potential then was 61.0% over this period. When down time for major system modifications is excluded, the total was 77.9%.

These major modifications involved three periods:

- October 7, 1974, to November 12, 1974, when a number of changes agreed among GM, EPA and ADL were implemented. Included were instrument recalibration, cleaning of control valves, installation of sample petcocks, installation of cake wash nozzles and investigation of chemical mix tank and clarifier overflow plugging problems.

- March 14, 1975, to April 15, 1975, when GM was investigating the sulfite plugging problem in the scrubbers. Ultimately, the scrubber operating mode was changed requiring some repiping of the recirculating and regenerated liquor lines.

- June 27, 1975, to September 8, 1975, when open trough lines were installed in the overflows of both chemical mix tanks and clarifier #1, all of which had plugged seriously at various times.

- March 5, 1976, to March 29, 1976, when a section of the regenerated liquor line was replaced along with a new orifice plate, both of which are intended to afford accurate flow monitoring at low flow rates relative to the original system design. At the same time, the instrumentation on the lime feed line was also being replaced to permit better control of the lime stoichiometry.

The test periods during which we monitored the system closely were:

- Intensive--August 19, 1974, to September 13, 1974

- Intensive--February 17, 1975, to March 14, 1975

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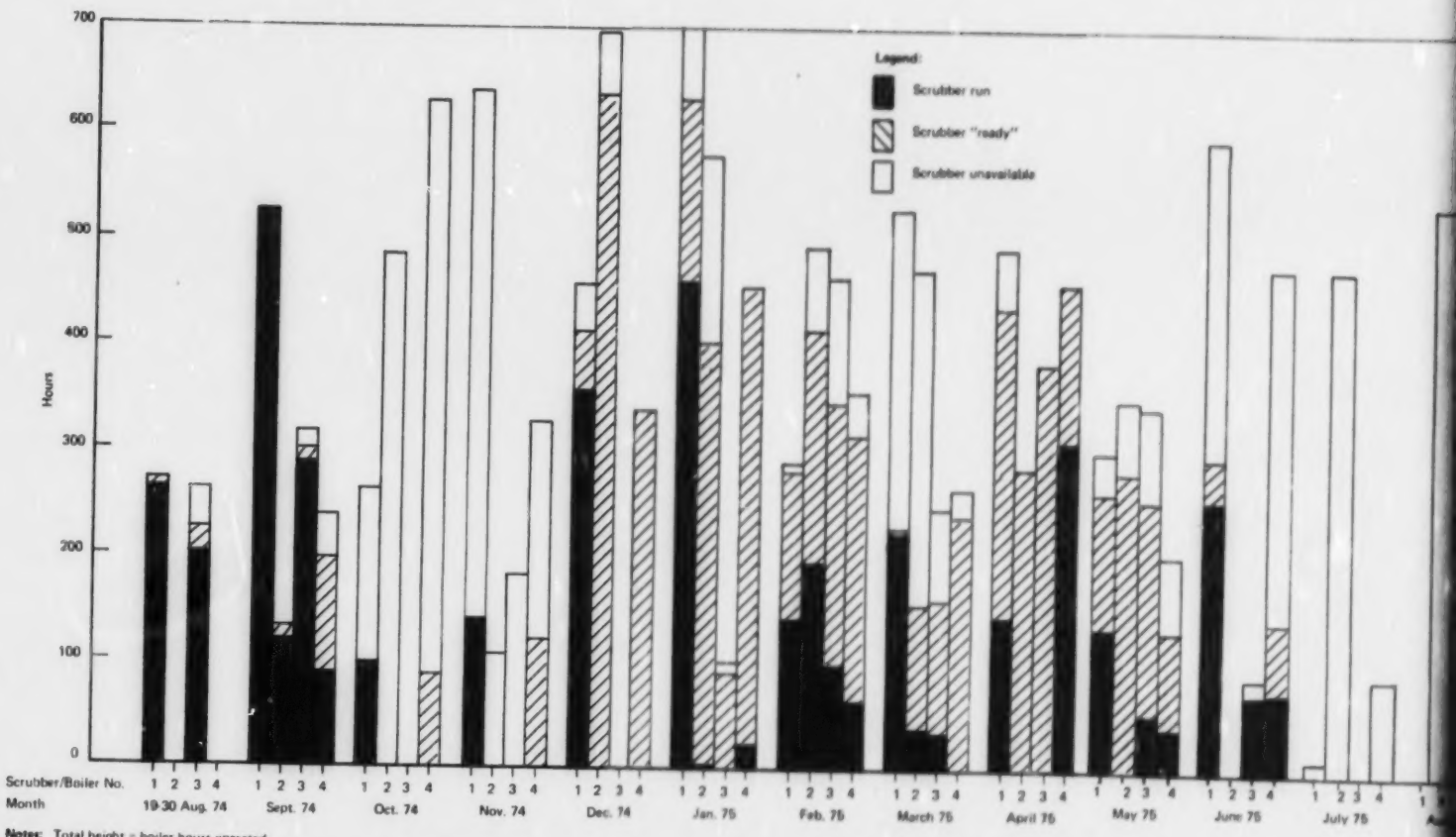

Notes: Total height = boiler hours operated.
Scrubbers control respective boilers only - no crossing over is possible.

FIGURE 3 SCRUBBER AVAIL

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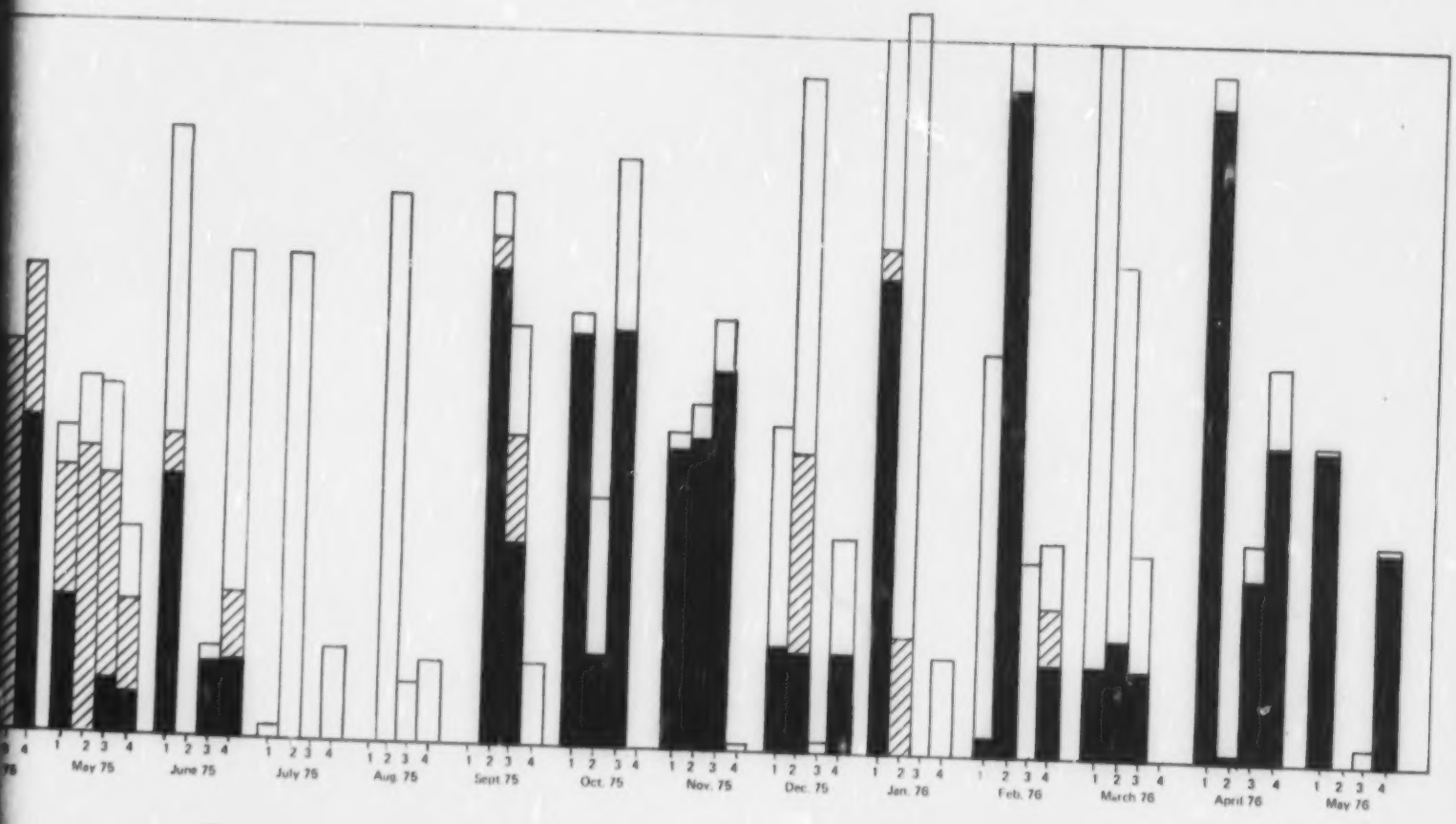

FIGURE 3 SCRUBBER AVAILABILITY

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- Non-Intensive--October 1975, to April 1976
- Intensive--April 19, 1976, to May 14, 1976.

In these various periods the operating flowsheets were different, notably in the locations at which the regenerated liquor entered the scrubber system and in the reactor system configuration. Figure 4 shows the original flowsheet when the regenerated scrubber feed entered the scrubber on the top tray while the recycle entered the scrubber separately, also on the top tray. Later (Figure 5), the regenerated liquor entered the recycle tank to mix with the liquor from the bottom tray. Next (Figure 6), the scrubber feed was mixed with the recycle liquor in the pipe prior to entering the scrubber to assure good mixing. Also during this period the filter cake was washed regularly, solids were recycled to chemical mix tank #1 from clarifier #1, and air was sparged into chemical mix tank #1 in an effort to improve solids properties by oxidizing the sulfur species to sulfate. Most recently (Figure 7), the scrubber feed system was unchanged and cake washing continued. However, the solids recycle was discontinued, lime was added to chemical mix tank #1 instead of #2, and oxidation by air sparging was performed in the scrubber bleed line upstream of the reactor.

Table 3 summarizes the important system operating parameters for the intensive test periods.

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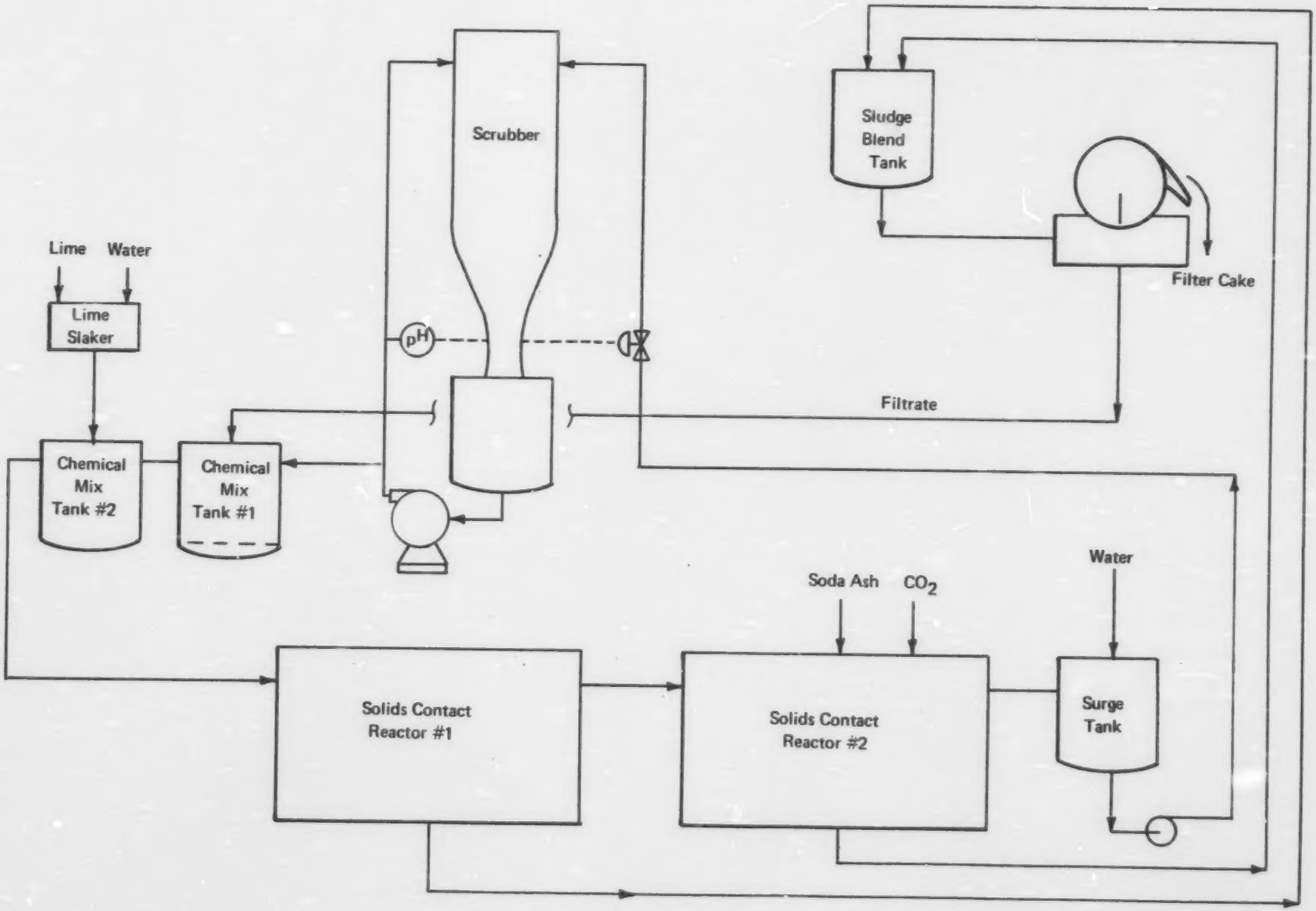


FIGURE 4 OPERATING FLOW DIAGRAM – 1ST INTENSIVE TEST

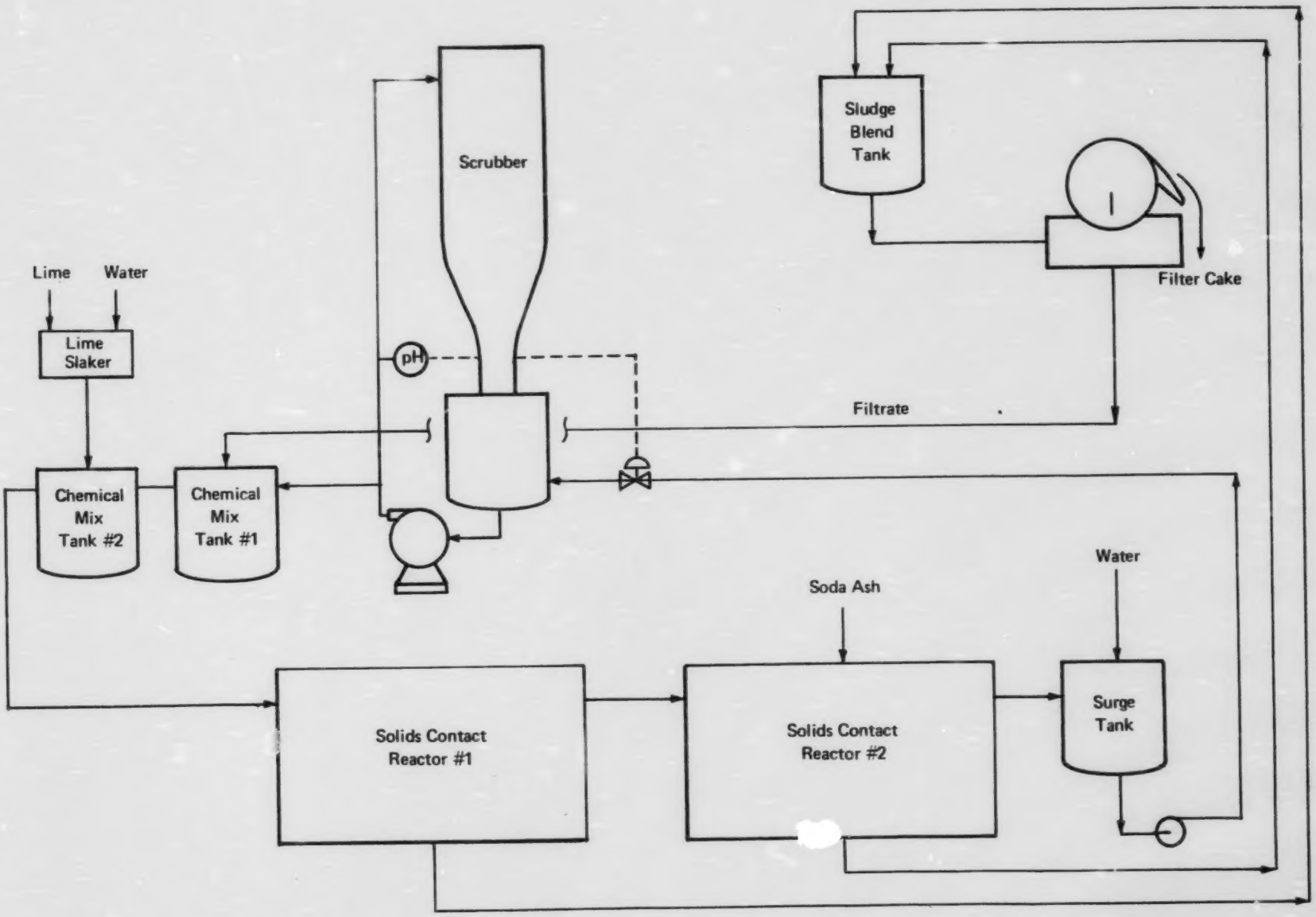


FIGURE 5 OPERATING FLOW DIAGRAM – 2ND INTENSIVE TEST

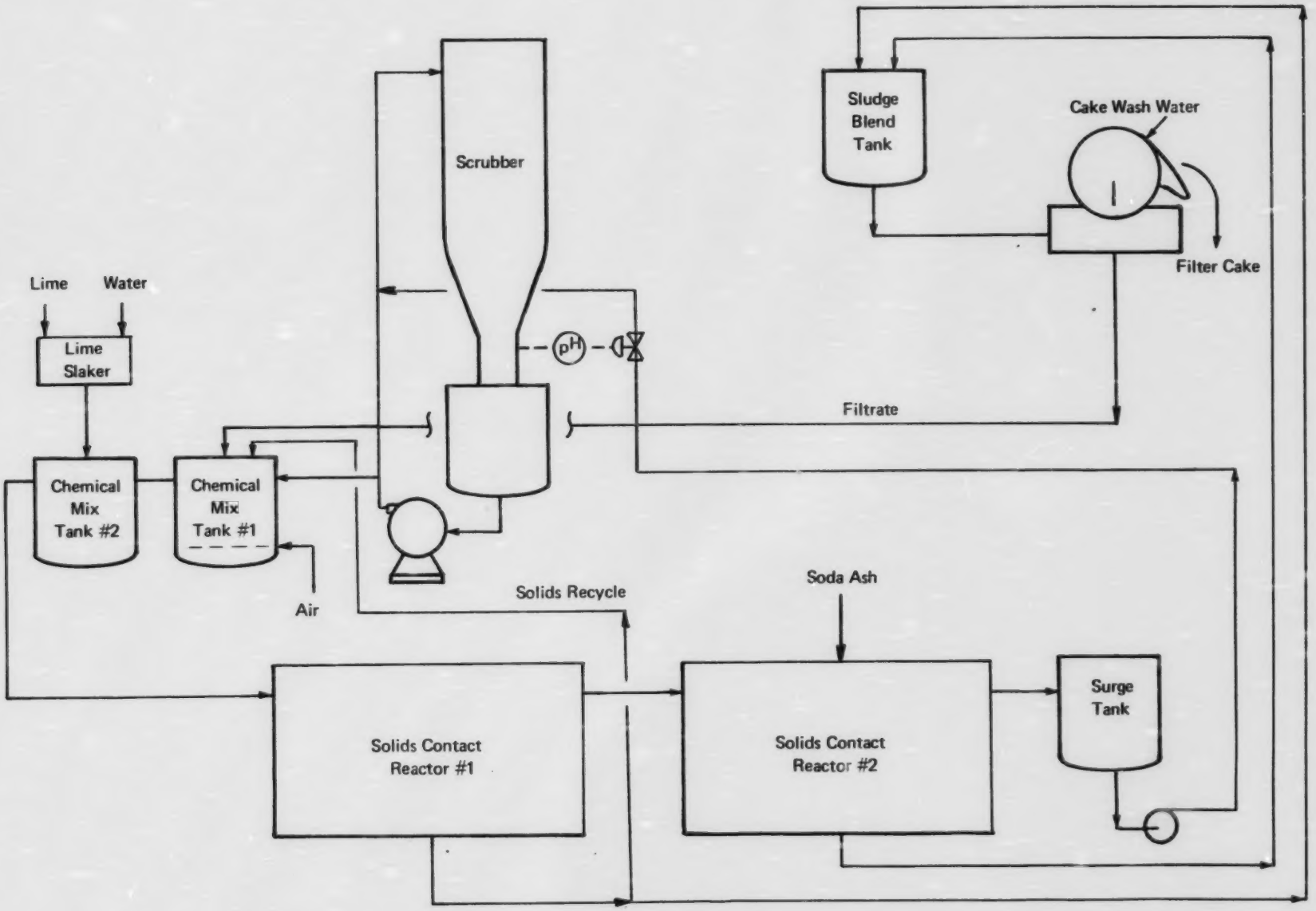


FIGURE 6 OPERATING FLOW DIAGRAM – NONINTENSIVE TEST

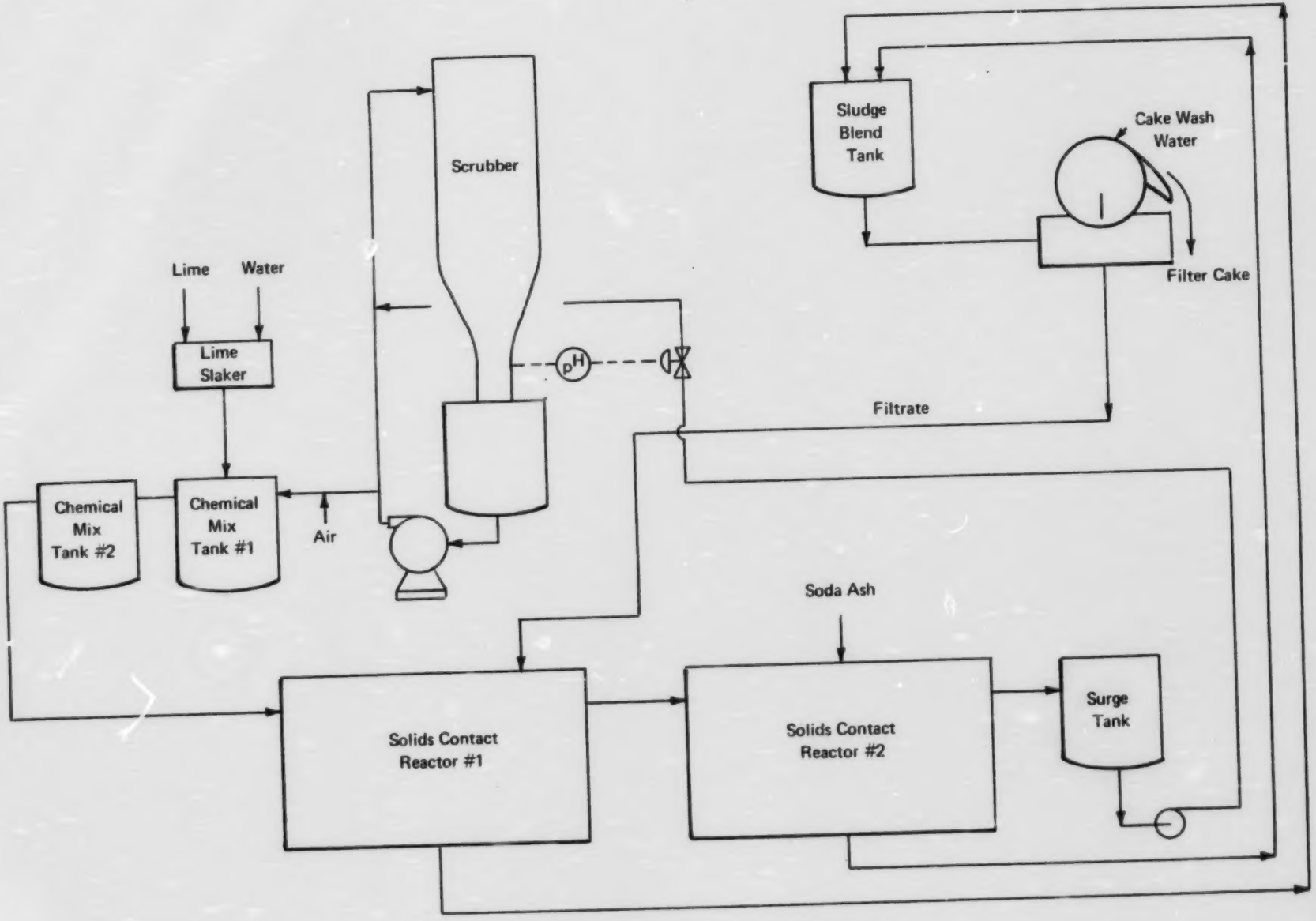


FIGURE 7 OPERATING FLOW DIAGRAM – 3RD INTENSIVE TEST

Table 3

SUMMARY OF AVERAGE OPERATING PARAMETERS

Test Period	8/19/74-9/13/74	2/17/75-3/14/75	4/19/76-5/14/76
Regenerated Liquor			
Na+, total, M	0.58	0.66	0.96
Na+, active, M	0.087	0.13	0.12
TOS*, M	0.004	0.010	0.009
OH^-, M	0.080	0.085	0.084
Ca++, M	0.0081	0.012	0.013
Cl^-, M	N.A.	0.12	0.18
Scrubber Bleed Liquor			
TOS*, M	0.021	0.37	0.033
H+, M	0.025	0.02	0.031
Suspended solids	<1.0	<1.0	<1.0
Chemical Mix Tank #2			
Suspended solids, wt.%	0.1-2.0	0.3	0.8
OH^-, M	0.1	0.09	0.07
Clarifier #1 Underflow			
Suspended solids, wt.%	18	16	13
Clarifier #2 Underflow			
Suspended solids, wt.%	35	13	29

* Total oxidizable sulfur.

IV. CHARACTERIZATION OF SYSTEM OPERATION

For intermediate or longer term operation (i.e., greater than about two times the system holdup), a reliable measure of several important system operating parameters, such as overall oxidation and lime and soda ash stoichiometries, is the filter cake composition. This is because virtually all chemicals fed to the system as well as the SO_2 removed from the flue gas leave via the filter cake.

Reflecting the load-following nature of the GM boilers, the operation during each test period was not steady because the number of scrubbers operated, SO_2 removal, the feed forward rate, chemicals makeup rate and solids filtration rate were variable over the periods. Consequently, the cake compositions were also variable, but less so because of the damping effect of the relatively long residence time of solids in the clarifiers. Therefore, although less reliable than in a steady period, filter cake composition is the most reliable basis available for quantifying the important parameters of operation.

Table 4 summarizes the average filter cake analyses for each test. The tolerances shown account for the variability in composition experienced over the one-month periods and reflect a 95% confidence level ($\pm$ two standard deviations of the mean). There are two components of variability which are included in the magnitude of the tolerances:

- actual changes in process operation affecting cake compositions; and
- analytical error.

Our experience with reproducibility of duplicate analytical results of this type indicates that most analyses are accurate to within 5% (95% confidence). Therefore, the major portion of the variability probably lies in the process operation. This confirms the conclusion of the overall material balance calculations (Appendix B) that in each test period there was no extended steady state operation.

The variability during the first intensive test was clearly greater than during the second. This is principally because during the first test the system operating rate was higher (with two scrubbers operating most of the time) and because solids were removed from the system much faster than they were produced (i.e., clarifier inventory was depleted). Therefore, with less opportunity for solids backmixing within the clarifiers, the composition of filter cake during the period was less uniform than during the second test when an average of one scrubber was on and solids were removed at a rate considerably lower than they were produced.

During the non-intensive test and again in the final intensive test, the variability of cake composition decreased. This was due in large part to the greater attention given to the system chemistry during the latter months of the test program. We found over the first week of the third

Table 4

MEAN FILTER CAKE COMPOSITIONS AND INDICATED OPERATING PARAMETERS

Test Period Intensive/Non-Intensive	(8/19/74-9/13/74) Intensive	(2/17/74-3/14/75) Intensive	(10/22/75-4/1/76) Non-Intensive	(4/19/76-5/14/76) Intensive
Composition of Total Cake, millimoles/gram dry cake				
Ca	7.03 ± 0.34	6.84 ± 0.10	6.66 ± 0.18	6.13 ± 0.24
SO_3	1.64 ± 0.42	2.23 ± 0.32	2.06 ± 0.28	0.63 ± 0.20
SO_4	2.37 ± 0.40	1.95 ± 0.24	2.09 ± 0.33	3.79 ± 0.17
OH	0.85 (by diff.)	1.66 ± 0.74	0.66 ± 0.33	0.73 ± 0.38
CO_3	3.00 ± 0.72	2.33 ± 0.48	2.70 ± 0.51	1.48 ± 0.34
Na	0.81 ± 0.12	1.01 ± 0.14	0.88 ± 0.23	0.26 ± 0.11
Composition of Insoluble Solids, millimoles/gram dry cake				
Ca	6.84 ± 0.41	6.80 ± 0.19	6.66	6.10 ± 0.24
SO_3	1.58 ± 0.37	2.07 ± 0.08	2.06	0.63 ± 0.20
SO_4	2.07 ± 0.66	1.45 ± 0.32	1.65	3.67 ± 0.17
OH	0.72 ± 0.31	1.17 ± 0.42	0.66	0.70 ± 0.38
CO_3	2.69 ± 0.75	2.08 ± 0.52	2.70	1.48 ± 0.34
Na	0[1]	0[1]	0[1]	0[1]
Composition of Soluble Solids, millimoles/gram dry cake[5]				
Ca	0.02 ± 0.002	0.047 ± 0.04	-	0.01 ± 0.001
SO_3	0.005 ± 0.0008	0.019 ± 0.017	-	0.001 ± 0.001
SO_4	0.329 ± 0.06	0.423 ± 0.046	0.44[3]	0.12 ± 0.01
OH	0.12 ± 0.012	0.163 ± 0.012	-	0.03 ± 0.01
CO_3	0[2]	0[2]	-	0[2]
Na	0.8 ± 0.10	0.98 ± 0.09	0.88[3]	0.26 ± 0.02
Lime Stoichiometry, Ca/SO_x in cake	1.90 ± 0.42	1.65 ± 0.14	1.69 ± 0.16	1.32 ± 0.106[4]
Soda Ash Stoichiometry, Na_2SO_x in cake	0.11 ± 0.02	0.12 ± 0.02	0.11 ± 0.021	0.028 ± 0.014[4]
Total Oxidation, SO_4/SO_x in cake	0.60 ± 0.08	0.47 ± 0.04	0.49 ± 0.065	0.83 ± 0.04[4]
Solids in Cake - Total Solids, wt.%	46.7 ± 3.0	40.9 ± 0.2	39.0 ± 3.57	56.0 ± 2.51
Soluble, wt.% as Na_2SO_4	2.5 ± 0.4	2.4 ± 0.3	2.4	1.0 ± 0.4
Insoluble, wt.%	44.2 (by diff.)	38.5 (by diff.)	36.6 (by diff.)	55.0 (by diff.)

Reported Tolerances are ± 2 Standard Deviations (95% confidence)

[1]Assumed equal to zero--i.e., assumed all Na ultimately leachable.
[2]Assumed equal to zero--too few analyses were performed.
[3]Assumed all Na_2SO_4--no filtrate analyses were taken.
[4]Reported for last three weeks of four week test--see text.
[5]Based on filtrate analysis.

intensive test that the cake properties changed rather rapidly to a point where the analyses remained relatively constant for the remainder of the test period. This indicates that the solids which were present in the clarifiers at the beginning of the test were probably different from those produced during the test. Therefore, in Table 4 the key operating parameters, lime and soda ash stoichiometries and oxidation, are summarized for only the last three weeks of the test.

Generally, the stability of these tests was sufficient to permit a characterization of the operating parameters of interest.

A. SO_2 Removal

Immediately prior to the test program, the system underwent a one-week test for SO_2 removal. The performance was excellent with removals in the range of 94-99% with relatively low inlet SO_2 levels of 600 and 1200 ppm, reflecting the high excess air, and some outlets as low as 20 ppm or less.

The periodic carbonate scaling on the top trays of the scrubbers in the initial mode of operation was attributed to poor mixing of regenerated and recycle liquors with resultant locally high pH's (Section IV-G). To counteract this problem, GM modified the piping so that the regenerated liquor would enter the recycle tank to ensure good mixing. This resulted in poor SO_2 removals ranging from about 20% to 85% with an overall average of 65%. SO_2 removal suffered because of the lower pH in the scrubber and the general loss of countercurrency (overall lower driving force). Further, there was calcium sulfite plugging,[1] which had not previously occurred.

As a result of this experience, GM reverted to essentially the initial flow scheme but with more efficient mixing of the liquors in a pipe outside the scrubber. SO_2 removals improved to the 90+% range immediately as the pH rose.

During the final intensive test we noted that the SO_2 removal in scrubber #1 was consistently somewhat lower than in scrubber #4. Number four is the older boiler with higher excess air and a consequently higher oxidation rate. Thus, a larger fraction of the SO_2 pickup is present in the liquor as SO_4 rather than SO_3. At the same controlled pH (6.0 on the bottom tray), the partial pressure of SO_2 above the solution is lower with higher oxidation, resulting in better SO_2 removal. General Motors performed an abbreviated test to determine if lowering the recycle rate of low pH material to scrubber #1 would have a noticeable effect on SO_2 removal by effectively increasing the mixed stream pH. Since the fractional change (about 20% reduction) in the recycle rate has a very small effect on the mix pH, the observed SO_2 removal was virtually unchanged.

[1]This plugging of scrubber trays, discussed later in Section IV-G, probably also contributed to the poor SO_2 removals as there was probably some gas channeling through the scrubber which inhibited mass transfer.

B. Filter Cake Properties

The quality of filter cake produced is measured in two ways:

- the total solids content of the cake which ultimately translates to the total weight of the sludge which must be hauled from the plant for disposal; and

- the soluble solids content of the cake which impacts directly on the environmental acceptability of disposing of the sludge as a landfill material.

The total solids (soluble plus insoluble) content in the filter cake for the periods summarized in Table 4 averaged 46.7%, 40.9%, 39.0% and 56.0%, respectively. For those produced in the first three periods, the fraction of solids in the cake was considerably lower than a reasonably expected level of 50%. Soluble solids in the cake of about 2.4-2.5% (wet basis) reflected the fact that no cake washing was performed during the first two test periods.

During the extended non-intensive test period, several other factors contributed to the solubles loss:

- the sodium concentration in the liquor loop increased substantially, to approximately the design level, by an average factor of almost two as compared with the first two intensive tests;

- at times the cake was not washed; and

- the low percent solids indicates a large moisture and solubles loss.

In the final period, improvement in solids properties was substantial. The cake contained 56% total solids of which only 1% was soluble on a wet basis. These are attributable to continuous cake washing, maintenance of low excess lime feed, and effective oxidation of the scrubber bleed.

C. Solids Dewatering Properties

During the first two tests the solids content of the filter cake was below expectation because of the excess calcium hydroxide in the cake and the relatively low concentration of gypsum ($CaSO_4 \cdot 2H_2O$). In an effort to counteract these effects, General Motors later adopted the flowsheet of Figure 6 for the non-intensive test period in which air was sparged into chemical mix tank (CMT) #1 to oxidize the sulfite/bisulfite which was not already oxidized in the scrubber system. Since this oxidation procedure lowers the pH by increasing the bisulfite/sulfite ratio, the stream must be at least partially neutralized to protect the mild steel reactors. The underflow from clarifier #1 was chosen for recycle to CMT #1 where both the alkaline solution and the excess hydroxide in the solid could neutralize the acidity. In addition, the presence of seed crystals would minimize

the possibility of sulfate supersaturation and subsequent scaling in CMT #2 and the clarifiers.

Unfortunately, poor solids settling and frequent solids overflow from the clarifiers resulted. Since the clarifiers were adequately sized to handle the flow from five scrubbers--and seldom were more than two operating on an extended basis--solids settling had never been an important problem, although flocculant was periodically used. Because solids recycled to the chemical mix tank from the clarifier underflow were carried in a three inch line in which a minimum velocity was required to prevent plugging, the total solids load on the clarifier increased several-fold as the solids concentration through the reactor-clarifier system increased to about 5% from the less-than-1% design level while the total volumetric flow was simultaneously increasing. The clarifiers, now experiencing hindered settling, were unable to handle this large duty, and solids carryover--to the extent that large quantities of flocculant were of no value--was the result.

In the third intensive test the solids recycle was eliminated. Oxidation upstream of the chemical mix tank apparently was effective. Slaked lime was added continuously to the first of two equal-size chemical mix tanks on the basis of periodic hydroxide analyses to avoid feeding excess lime. Thus, with good-settling gypsum crystals and less unutilized lime, the solids produced in the third intensive test were consistently the driest observed. And for the first time, GM discontinued the use of flocculant.

D. Lime Stoichiometry

The consumption of lime during the entire test program, while improving, has been significantly greater than theoretical. Lime stoichiometry values of 1.90, 1.65, 1.69 and 1.32 moles Ca per mole SO_2 removed were observed for the four individual test periods. Because of difficulties with the automatic lime feed control system (plugged control valve, scaled magnetic flowmeter, etc.), the operators have been forced to feed lime to the system under manual control.

The method of controlling the lime feed rate coupled with the low sodium level in the system contributed to the poor utilization in the first two tests. Lime was fed to the chemical mix tank on the basis of the target hydroxide level of 0.1M OH^- in the scrubber feed. At an Na_2SO_4 concentration of 0.33M, the solubility of hydroxide is somewhat less than this target value. Thus, overfeeding of lime was common, since a large increase in the feed rate results in a small, if any, increase in the hydroxide level.

The lime feed control method during the non-intensive test was to manually adjust the lime feed rate in proportion to the rate of regenerated liquor sent to the scrubbers assuming the target 0.1M hydroxide was met. However, considerable difficulty was experienced, not because the principle was not sound, but because the scrubber feed rate--the critical variable--could not be measured accurately. Finally, before the third intensive test, the flow orifice and a section of pipe were replaced to obtain good flow indication.

In the third intensive test the lime feed (again manually controlled) was set to give a [OH^-] in chemical mix tank #2 of about 0.08-0.09M. This has worked best of any method to date at GM, resulting in a lime stoichiometry of 1.32 for the period, somewhat higher than the target of 1.2 (set by GM, EPA and ADL for this program).

E. Carbonate Softening

As discussed earlier, some degree of softening is necessary before the regenerated liquor is returned to the scrubber loop to avoid the potential for solids deposition there. The soluble calcium level for the liquor entering the softening clarifier has been about 800 ppm by weight, and was reduced to the 350-550 ppm range depending on the operating mode, the evidence and recent history of plugging, and the source of carbonate for softening.

By the end of the test program, when most operating parameters were within expectation, the softening was performed to reduce Ca++ concentration to a level of 500 ppm continuously, resulting in no evidence of plugging. It is not yet clear what maximum level of soluble calcium can be tolerated. However, since the degree of softening directly impacts on the consumption of soda ash (Section IV-F), it is important that softening be minimized to reduce operating costs and reduce the soluble sodium salt content in the waste solids.

The General Motors system has provisions for using either of two carbonate softening agents, carbon dioxide or soda ash. The use of gaseous carbon dioxide was attempted to various extents for the first year of system operation. The principal drawback of this approach was found to be the fact that CO_2 addition neutralized two moles of alkalinity per mole of calcium precipitated. This lowered the capacity for SO_2 removal unless the scrubber feed rate was correspondingly increased. Further, GM reports that the dewatering properties of the CO_2-precipitated solids were inferior to those produced from soda ash. As a result, GM has discontinued regular use of CO_2 and has it available only as a contingency.

Soda ash softening is far more effective. No neutralization of liquor alkalinity occurs and the solids settle and filter well. One area requiring caution is that of controlling the sodium balance as discussed below.

F. Soda Ash Stoichiometry

As reported in Table 2, the solubles loss for the early test periods was in excess of 0.1 moles Na_2 per mole SO_x removed. This is relatively high, reflecting the fact that the filter cake was not washed. Despite washing which had begun by October, 1975, the soda ash stoichiometry remained excessive because of: (1) high total sodium (>1.2M) in the liquor requiring more washing; (2) occasionally unwashed samples which hurt the overall average; and (3) high liquor content in filter cake increasing the moisture and solubles losses.

During the last month of the test program, there was a very low solubles loss, about 0.03 moles of Na_2 per mole of SO_x removed, which is lower than the General Motors design level of 0.05. This demonstrated the system's ability to achieve a significant reduction in soluble solids by cake washing.

However, there was a buildup of sodium in the system over this test period as reflected by the higher rate of sodium input (as soda ash) than the rate of removal (as soluble solids losses in the filter cake), and by the increase in concentration of sodium ion over the period. Therefore, this is not a steady state mode of operation.

System operation to date indicates that the filter cake can be washed to levels resulting in sodium loss rates which are lower than minimum sodium makeup rates required for soda ash softening (Table 5). Therefore, it would be misleading to indicate that a soda ash stoichiometry of 0.03 has been achieved based only on filter cake data. Since the minimum level of softening has not yet been determined, the theoretical minimum soda ash stoichiometry cannot yet be projected. However, if the softening requirement can be lowered to a Ca++ reduction of 150 ppm, the soda ash stoichiometry would drop to about 0.05. The system has not yet been operated at a Ca++ reduction of less than 250 ppm for an extended period.

G. Scaling in Scrubber Loop

Operation of the General Motors Double Alkali system during testing has encountered two sets of circumstances leading to buildup of solids in the scrubber loop. Prior to the program, GM noted on several occasions the buildup of calcium carbonate scale on the top tray of the scrubber. The flowsheet at these times was as the scheme in Figure 4 with the scrubber feed entering the top tray directly and mixing with the recycle stream upon the tray. The fact that $CaCO_3$ scale was in fact formed on the top tray is indicative of incomplete mixing of the liquid streams and locally high pH levels capable of scrubbing CO_2 from the flue gas.

After some experimentation to correct the carbonate scaling, GM adopted the flow scheme of Figure 5 (Chapter III). In this configuration, solids plugged the trays with calcium sulfite. Plugging occurred because: (1) the pH in the recycle tank was about 7.5 (versus 6.0 in the other tests), therefore, the TOS was mostly sulfite; (2) the soluble calcium level was 400-500 ppm; (3) the total sodium concentration of about 0.33M Na_2, about 30-40% below the design concentration, resulted in a low ionic strength of about 1.0; and (4) the concentrations of these species exceeded the apparent solubility product for calcium sulfite of about 4×10^{-5} in the solution.

Supersaturation of the solution in the recycle tank resulted in precipitation in the scrubber system. Plugging was predominant in areas

Table 5

SODIUM BALANCE DATA

SOFTENING VS. SOLUBLES LOSS

Date	4/26-30/1976	5/3-7/1976
Regenerated liquor flow, m^3/hr(gpm)	44(193)	44(193)
Soluble calcium - unsoftened, ppm	880	800
softened, ppm	520	440
SO_x removal rate, kg-mole/hr (lb-mole/hr)	3.00(6.59)	3.10(6.81)
Calculated calcium precipitation mole Ca/mole SO_x removed	0.13	0.13
Soda ash makeup rate, mole Na_2/mole SO_x removed	0.12	0.11
Filter cake solubles, mole Na_2/mole SO_x in cake	0.056	0.01

of maximum SO_2 absorption; i.e., in the vicinity of the valve slots on the trays. Plugging also occurred in the quench nozzle where the relatively high temperature (350°-550°F) of the untreated flue gas may have played a role.

After this sulfite scaling experience, GM reverted to the flow scheme where regenerated liquor enters the top tray along with recycle liquor--with one major modification. The streams mix entirely outside the scrubber in a length of recycle pipe. This assures good mixing and avoids the local carbonate scale problem of the earlier operating days. This mode has worked well showing no tendency to scale at normal operating pH.

H. Oxidation

The overall oxidation rates apparent from the filter cake analyses were about 60% in the first period and 47% in the second. This is as expected since in the first test period the scrubbers operated principally were #1 and #3 and in the second #1 was operated predominantly. Boiler #3 is one of the older boilers and operates with considerably more excess air than #1 resulting in greater oxygen pickup by the scrubber liquor and hence more oxidation.

Another factor which may have contributed to lower oxidation rates in the second test period was that the sulfur content of the coal was probably higher. The average sulfur value of the coal purchased in August and September 1974 was 2.36%. In February 1975 it was 2.48%. In the latter period, flue gas SO_2 analyses were taken almost daily and indicated that, on average, the coal actually burned was nearer 3.0% sulfur. Thus, the oxidation rate as a fraction of SO_2 removal decreased as the SO_2 removal increased. Flue gas analyses were not performed during the August-September 1974 period.

In the non-intensive period the average oxidation rate was about 49%, consistent with that of the second intensive test. Since boilers #1 and #2, the newer ones, carried most of the load for this six-month period, scrubber oxidation was in the lower range.

During this period, air was being sparged into chemical mix tank #1 while solids were being recycled as well (Figure 5). This proved rather ineffective for a combination of several possible reasons:

- there was no provision for measuring the total air flow which may in fact have been quite low;

- although the sparger design (two perforated pipes) appeared to be adequate, the gas-liquid interface for oxygen mass transfer may not have been adequate; and

- with the presence of recirculated solids containing a considerable quantity of unutilized alkalinity, the sulfite and bisulfite may have been substantially precipitated before having sufficient opportunity to oxidize.

In the final test period the cake analyses indicated an average overall oxidation rate of about 83%. From the material balance data of Appendix B, a scrubber oxidation rate of about 55% was apparent, which was quite consistent with earlier periods. The remaining oxidation occurred in the newly installed sparger in the scrubber bleed line upstream of the chemical mix tanks.

I. Entrainment

Isolated instances of high entrainment from the scrubbers were observed during the first intensive test as evidenced by considerable dense mist emerging from the scrubber stacks and carrying down from the roof to the ground. As a result, it was decided to measure entrainment in the scrubber flue gas effluent. This entrainment test, performed by Crobaugh Laboratories on January 14-16, 1975, showed entrainment of 19.5 and 16.8 liters per hour (5.16 and 4.43 gallons per hour) from scrubbers #1 and #4, respectively.

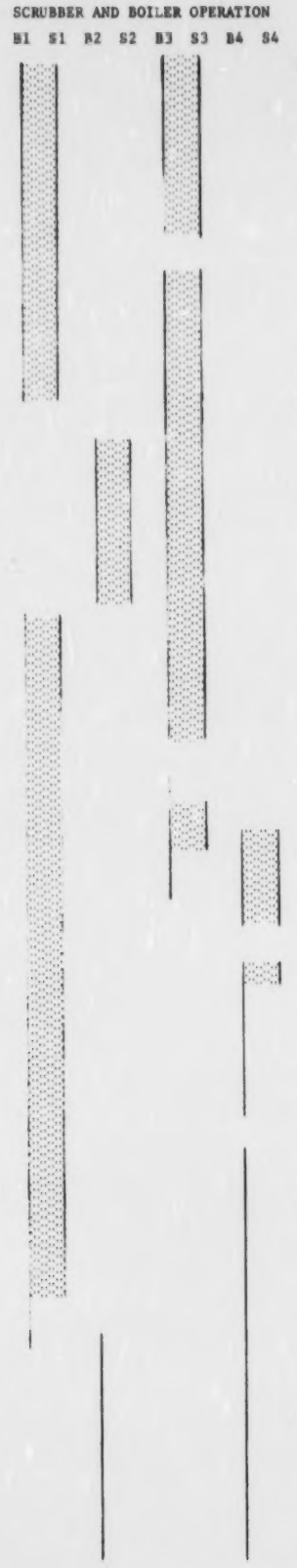
Although entrainment of scrubber liquor is within the design specification, the total potential entrainment of soluble solids (assuming 0.5M Na_2SO_4), is about 1.4 kg/hr or 0.013 gm/Nm^3 (3 lb/hr or 0.012 grains/scf). Based on a heat input of 20 x 10^6 Kcal/hr (80 x 10^6 Btu/hr) to the boiler, the code restricts the particulate emissions to about 7.3 kg/hr (16 lb/hr), depending on the boiler operated. Therefore, soluble solids lost as entrainment from this system can contribute significantly to the allowable particulate emissions.

A contributing factor to the periodic entrainment problem is the location of the demister relative to the transition piece at the top of the scrubber. Immediately above the full-diameter demister pad, is a square reducer through which the outlet gas passes into a high velocity duct. Inspections during shutdowns of solids buildup on the pad indicate that the gas is to a large extent not "seeing" the full diameter but is making the transition upstream of the demister, thereby rendering much of it ineffective.

Over the past few months the stainless steel wire mesh entrainment separators have been replaced as necessary with plastic mesh pads of the same size. These polypropylene units are expected to outlast the original equipment which deteriorated seriously over time. Although there is no reason to believe that these plastic mist eliminators would work more effectively than the original wire ones, there has been little visual evidence in recent months of any entrainment problems. Further, the sodium balances have closed well indicating little, if any, loss via entrainment.

APPENDIX A

SUMMARY OF SCRUBBER AND BOILER OPERATION



8-19-74 --- Recently installed weir block on top tray of scrubber #3 to avoid local scaling. Began first intensive test.

20 --- Sump pumps kicking on causes CMT #1 overflow. Entrainment problem--mist elim. requires testing. Some instruments require recalibration, new relays.

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9- 1-74

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13 --- Ended first intensive test.

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10-1-74

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7 --- System down for modifications agreed among EPA, GM and ADL.

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9

10

11 --- Scrubber feed control (on pH) - changed from multiplier to adder - should be log not linear. #1 SCR turbine under repair. CMT #1 overflow plugged - probably during intensive test period. Scrubber feed pressure regulator had not been operating properly - has just been cleaned.

12

13

14

SCRUBBER AND BOILER OPERATION

B1 S1 B2 S2 B3 S3 B4 S4

10-15-74
16
17
18
19
20
21
22
23
24
25
26
27
28
29 --- Still down-plugged #1 SCR overflow. Open trough overflow from SCR #1-#2
30 contemplated. Trying to add scrubber feed to recycle tank. Valve in
31 CMT #1 overflow line removed and line repiped to avoid future plugging.
11- 1-74
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19 --- Clarifier #1 overflow plugged. System has been run with no lime
20 addition only Na_2CO_3 added to bring Na^+ level up.
21 ---
22
23
24
25
26
27
28
29
30
12- 1-74
2
3
4
5
6
7
8
9
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11
12
13

SCRUBBER AND BOILER OPERATION

12-14-74
15
16
17
18
19 --- Limited operation during holiday period.
20
21
22
23
24
25
26
27
28
29
30
31
1- 1-75
2
3
4
5
6
7
8
9
10
11
12
13 --- Entrainment test with Koch present. Reported scrubber #1 - 5.16 gal/hr. Reported scrubber #2 - 4.43 gal/hr. Running w/ Na_2CO_3 makeup only.
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
2- 1-75 -- Scrubbers down for weekend.
2
3
4 --- All scrubber feeds repiped - recycle tank.
5
6
7
8
9
10
11
12

SCRUBBER AND BOILER OPERATION

B1 S1 B2 S2 B3 S3 B4 S4

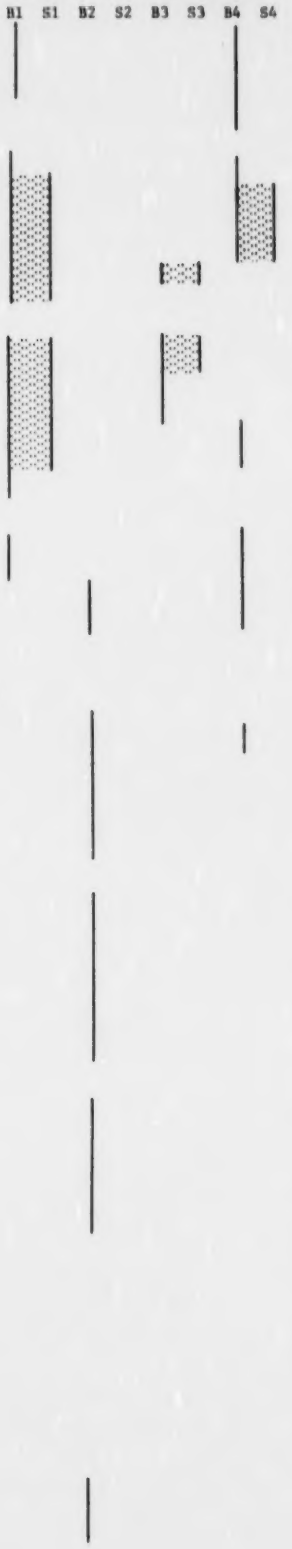
2-13-75
14
15
16
17 —- Began second intensive test.
18
19
20 —- #3 scrubber - plugged trays. #2 shutdown - some pluggage of trays.
21 —- Scrubbers down for weekend--manpower shortage.
22
23
24
25
26 —- Scrubber #2 still down - #3 and #4 plugging on lower trays. Filter
27 wash not resumed: poor vac., may need new pumps - belt pulls apart,
28 solids in underflow quite low - poor release properties.
3- 1-75
2
3
4
5
6
7
8 —- Scrubbers down for weekend--manpower shortage.
9
10
11
12
13
14 —- Solids analysis of scrubber #2 bottom of tray 1 - 24.6% $CaSO_3$, 1/2
15 H_2O, quench nozzle - 70.8% $CaSO_3$, 1/2 H_2O. Ended second intensive
16 test--scrubbers down during investigation of scrubber plugging
17 problem.
18
19
20
21
22
23
24 —- Attributing poor SO_2 removal to $CaSO_3$ scaling in scrubbers. Precip.
25 seems time delayed.
26
27
28
29
30
31
4 -1-75
2
3 —- #1 up at 10:30 4/1 - down 4/3 12:30; attempting to run low liquid
4 level in recycle tank and cavitated pump.
5
6
7
8 —- This and following run of 4/15/75 somewhat experimental in new
9 mode of scrubber pH control.
10
11
12
13
14

SCRUBBER AND BOILER OPERATION

--- Overflowed solids into system. Running on bottom tray pH = 6.3. Some cake washing. Still trying to get Na+ up.

--- Plugged; chemical mix tank #2 overflowed.

SCRUBBER AND BOILER OPERATION



6-11-75
12
13
14
15
16 --- System restarted after chem. mix tank #2 overflow bypassed.
17
18
19
20
21
22
23
24
25
26
27 --- System down for installation of open-trough overflow lines.
28
29
30
7-1-75
2
3
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14
15
16
17
18
19
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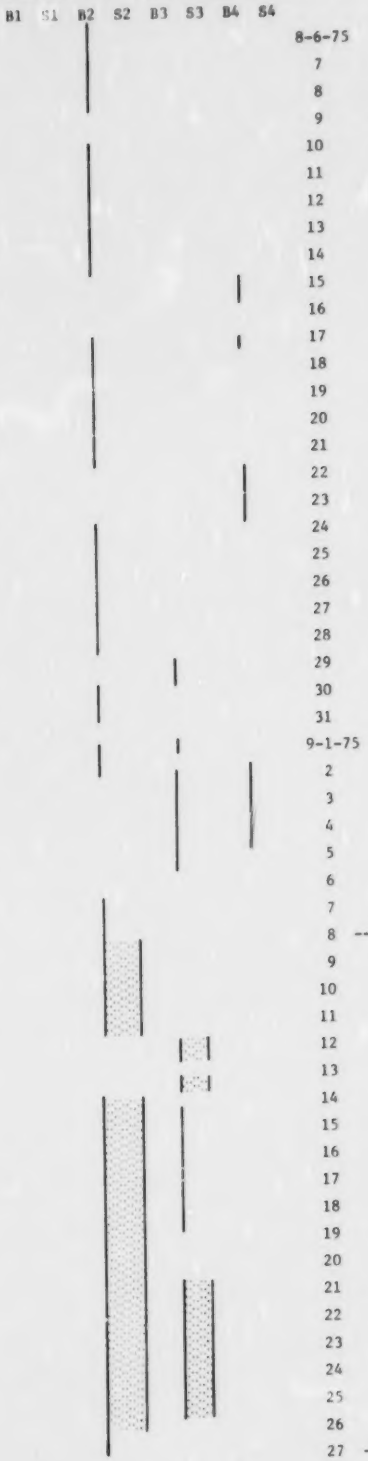
21
22
23
24
25 --- Annual shutdown.
26
27
28
29
30
31
8-1-75
2
3
4
5

SCRUBBER AND BOILER OPERATION



8-6-75
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17
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21
22
23
24
25
26
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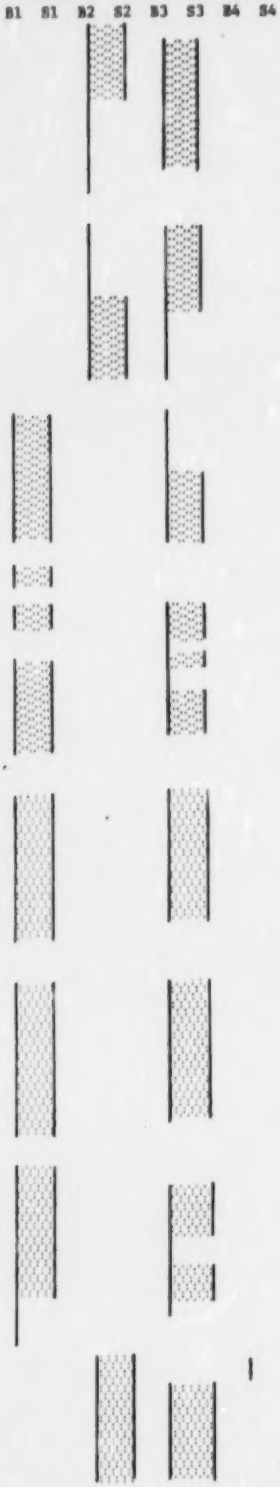
28
29
30
31
9-1-75
2
3
4
5
6
7
8 --- System restarted with open trough overflow lines.
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27 --- #2 ID fan vibrating.

SCRUBBER AND BOILER OPERATION

B1 S1 B2 S2 B3 S3 B4 S4



9-28-75
29
30
10 -1-75 -- #1 scrubber plugged due to solids recycle.
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16 --- #3 bleed line plugged--3 hours.
17
18
19
20 --- Solids carryover.
21
22
23
24
25
26
27
28
29
30
31
11 -1-75
2
3
4
5
6
7
8
9
10
11 --- Solids carryover.
12
13
14 --- Solids carryover.
15
16
17
18
19
20

SCRUBBER AND BOILER OPERATION

11-21-75
22
23
24
25 --- Solids carryover.
26
27
28
29
30
12 -1-75 - #3 quench line leaking - cannot start up.
2 --- Solids carryover.
3
4
5
6
7
8
9
10 --- Solids carryover.
11
12
13 --- Solids carryover.
14
15
16
17
18
19 --- Down for holidays; catching up on solids filtration.
20
21
22
23
24
25
26
27
28
29
30
31
1 -1-76
2
3
4
5
6
7
8
9 --- Solids carryover.
10
11
12

SCRUBBER AND BOILER OPERATION

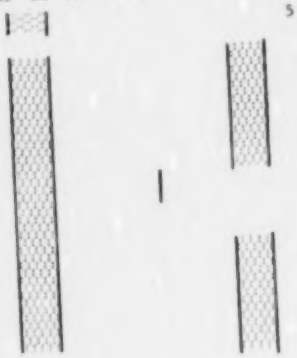
1 '3-76
14
15
16
17
18
19
20
21
22 --- Solids carryover.
23
24
25
26
27
28
29
30 --- Solids carryover.
31
2 -1-76
2
3
4
5
6
7
8
9
10
11
12
13 --- #4 scrubber plugged.
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
3 -1-76
2
3
4
5 --- Down for scrubber feed and lime feed instrumentation changes.
6

SCRUBBER AND BOILER OPERATION

3 -7-76
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
4 -1-76
2
3 --- Leak in #1 scrubber bleed line.
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18 --- #1 booster fan vibrating; foundation cracked; #2 demist. plugged,replaced.
19 --- Intensive test no. 3 began.
20
21
22
23
24
25 --- Took 5 hours to start booster fan--electrical problem.
26
27
28
29
30

SCRUBBER AND BOILER OPERATION

B1 S1 B2 S2 B3 S3 B4 S4



5 -1-76

2

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4

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12

13

14 --- End test program.

APPENDIX B

MATERIAL BALANCES

APPENDIX B

MATERIAL BALANCES

A. Overall and Component Material Balances

We ran material balances for the overall system and for component systems to check the validity and consistency of the various measurements of flow and composition made during the three intensive test periods. In planning the data acquisition program we viewed the first intensive test period as one of orientation. Only the instrumentation initially incorporated into the plant design was recommended for use. If the test results showed that additional or more accurate data collection were necessary or that minor equipment or instrumentation revision were required for the success of future tests, such modifications would be undertaken.

Although no flue gas measurements were made in the first test--they had been made one month earlier--and the filter cake was not weighed, the material balances performed (and discussed below) appeared consistent. For the second and third intensive tests these measurements were made regularly and provide the definitive material balance basis upon which to draw appropriate conclusions.

Ideally, to minimize the difficulties in closing material balances, the system is best tested at steady state. This, however, is not practical from the standpoint of the constraints of meeting the variable steam requirements of a manufacturing complex and weekend shutdowns for energy conservation. Therefore, it was not unexpected that the system experienced no long steady-state periods during the tests.

1. One-Month Intensive Test Balances

Over each intensive test period a total (liquid + solids) balance was attempted. Thus, ignoring the oxygen for oxidation and assuming no net CO_2 absorption,

SO_2 absorbed + Lime + Water + CO_2 addition + Na_2CO_3 = Wet Cake + Evap.

For Intensive Test Period No. 1 (8/19/74 through 9/13/74), this balance was not performed as all the necessary data was not collected for reasons discussed above. With appropriate estimates, the balances shown in Table B-1 were made for calcium, sodium, and carbon. These balances show that during the 26-day period, the system inventory was not constant as more calcium, sodium and carbon was removed than was fed.

For Intensive Test Period No. 2 (2/17/75 through 3/14/75), Table B-2 shows that the system seemed to be accumulating solids and sodium,[1] but to be closer to overall balance than in the previous test period.

---

[1] This apparent buildup of sodium is at least partly offset by overflow losses from the chemical mix tanks and clarifiers, which although known to have occurred are not quantifiable.

Table B-1

GM PARMA PLANT

ONE-MONTH OVERALL BALANCE--INTENSIVE TEST PERIOD NO. 1

8/19/74 through 9/13/74

Measured Inputs

CaO	111,700 kg
H_2O (liquid)	5,352,100
CO_2	14,600
Na_2CO_3	3,300
	5,481,700 kg

Measured Outputs

Wet Cake: 995,700 kg (est. from Clarifier Underflows)

Cake Composition: 47.1% Solids Containing

7.03 m Moles of Ca^{++}/g Dry Solids	
1.64	$SO_3^=$
2.37	$SO_4^=$
3.00	$CO_3^=$
0.81	Na^+
0.85	OH^-

Balances

	Inputs (I)	Outputs (O)	(O - I)/I
Ca	79,800 kg	131,900 kg	+ 65%
Na	1,440	8,740	+508%
C	4,350	16,900	+288%

Note: Elemental C balances exclude CO_3 in lime which analyses showed to be negligible.

Table B-2

GM PARMA PLANT

ONE-MONTH OVERALL BALANCE--INTENSIVE TEST PERIOD NO. 2

2/17/75 through 3/14/75

Measured Inputs

SO_2	84,800 kg
CaO	76,300
H_2O (liquid)	3,364,400
CO_2	3,700
Na_2CO_3	11,800
	3,541,000 kg

Measured Outputs

SO_2:	29,400 kg
Wet Cake:	309,600
	339,000 kg

Cake Composition: 41.4% Solids Containing

6.84	m Moles of Ca^{++}/g Dry Solids
2.23	$SO_3^=$
1.95	$SO_4^=$
2.33	$CO_3^=$
1.01	Na^+
1.66	OH^-

Balances

1. Evaporation by Overall Balance (1)

   = 3,541,100 - 339,100 = 3,202,000 kg (22.7 gal/min)

2. Elemental Balances

	Inputs (I)	Outputs (O)	(O - I)/I
Ca	54,500 kg	35,100 kg	-36%
S	42,400	31,900	-25%
Na	5,100	3,000	-42%
C (2)	2,360	3,580	+52%

(1) Agrees with psychrometric calculations.

(2) Elemental C balances exclude CO_3 in lime which analyses showed to be negligible.

For Intensive Test Period No. 3 (4/19/76 through 4/15/76), Table B-3 shows an overall net accumulation of solids in the system, mainly sulfur salts in clarifier #1 while carbonate was being depleted from clarifier #2. As shown in the next section, the middle two weeks of the test program were relatively steady material balance periods. Net accumulation of solids occurred mainly during the final week of testing at reduced filtration rates. The accumulation of sodium in the system agrees with the measured increase of total sodium concentration in the liquor from .935 M to .987 M over the two one-week short-term material balances.

2. Short-Term Intensive Test Balances

The approach taken in reducing the raw data for short-term intensive test material balances was to determine the relatively steady periods of operation by appropriately plotted and tabulated operating data and analyses. These were three to five day periods in each case. For a selected portion of an intensive test period, measurement of all the streams noted in Figure B-1 would allow complete balances to be run on all three systems shown in Figure B-1.

To complete the material balance for the selected steady period of Intensive Test Period No. 1 (8/27/74 through 8/30/74) we made several assumptions. The scrubber feed rate was estimated at 23 m^3/hr (100 gpm--the flow was normally in this range and the estimate corresponded to reasonable evaporation and SO_2 pickup rates). The scrubber bleed flow was then estimated by assuming a sodium balance across the scrubber. Since the wet cake weight was estimated from the clarifier underflows and there is no filtrate flow meter, balances were estimated. SO_2 removal and evaporation could be estimated based on liquor flows as shown in Table B-4. Table B-4 confirms that the system was probably losing inventory but that the loss was not as serious over the 4-day material balance period as it was over the month-long test period.

The balances for the selected portion of Intensive Test Period No. 2 (2/26/75 through 2/28/75), as expected, were more complete. The only assumptions required were that:

- the outlet water content of the flue gas was estimated based on saturation at scrubber gas outlet temperature; an adiabatic saturation line on the air-H_2O psychrometric chart was used to estimate inlet humidity;
- again, the scrubber bleed flow was estimated from a sodium balance across the scrubber after a reasonable estimate of the scrubber feed; and
- the filtrate flow and solids content were estimated from the cake and clarifier underflow measurements.

The balances for the second period are summarized in Table B-5. They confirm a small accumulation of material inventory during the test period.

Table B-3

GM PARMA PLANT

LONG-TERM OVERALL BALANCE--INTENSIVE TEST PERIOD NO. 3

4/19/76 through 5/14/76

Measured Inputs

SO_2	96,800 kg
CaO	92,800
H_2O (liquid)	3,481,200
Na_2CO_3	20,000
	3,690,800 kg

Measured Outputs

SO_2:	10,600 kg
Wet Cake:	309,400
	320,000 kg

Cake Composition: 56.0% Solids Containing

6.13	m Moles of Ca^{++}/g Dry Solids
0.63	$SO_3^=$
3.79	$SO_4^=$
1.48	$CO_3^=$
0.26	Na^+
0.73	OH^-

Balances

1. Evaporation by Overall Balance (1)

   = 3,691,000 - 319,900 = 3,371,100 kg (24.7 gal/min)

2. Elemental Balances

	Inputs (I)	Outputs (O)	(O - I)/I
Ca	66,300 kg	43,800 kg	-36%
S	48,500	24,500	-50%
Na	8,670	1,040	-88%
C (2)	2,260	3,080	+36%

(1) Agrees with psychrometric calculations.

(2) Elemental C balances exclude CO_3 in lime which analyses showed to be negligible.

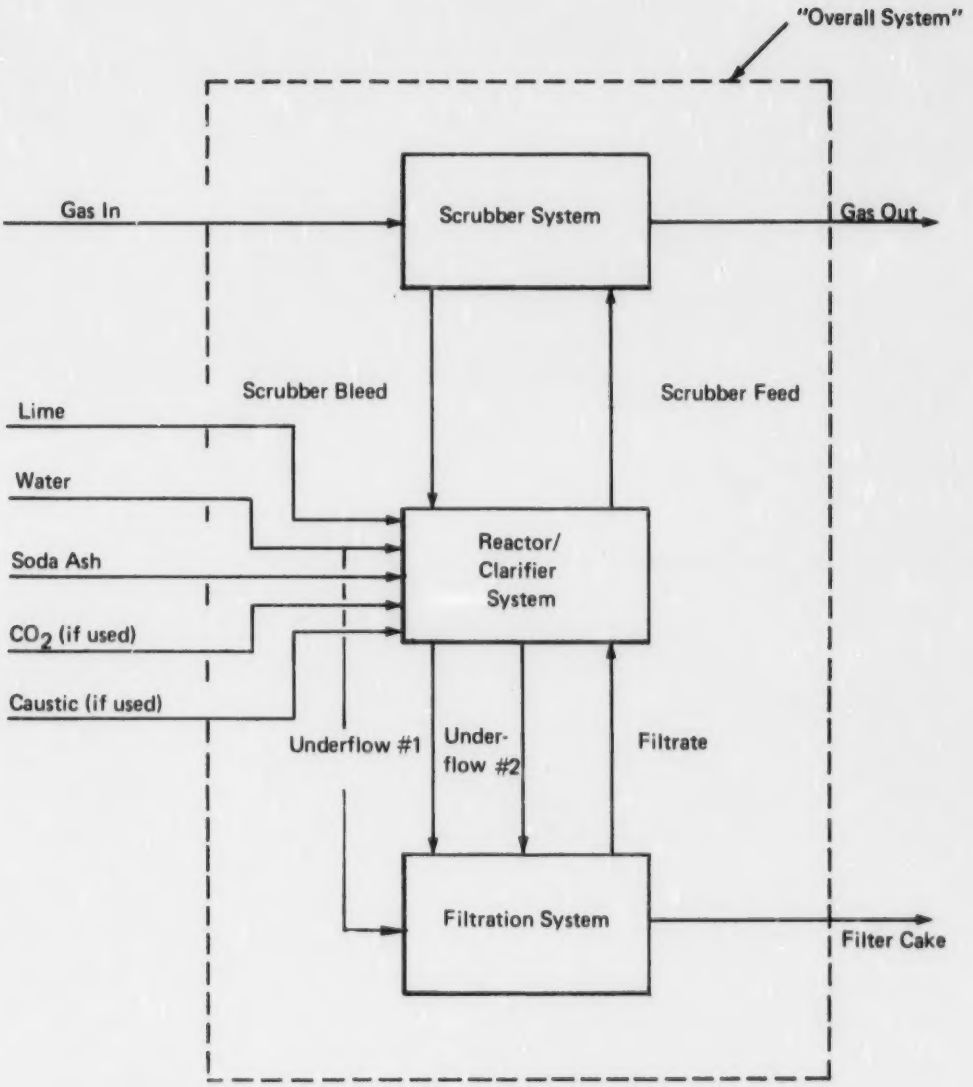

FIGURE B–1 DEFINITION OF TERMS – GM SYSTEM

Table B-4

SUMMARY OF SHORT TERM BALANCES - AUGUST 27-30, 1974

	kg/hr		
	Total Input (I)	Total Output (O)	Difference (O - I)/I, %
Scrubber System			
Total Flows	38,400	38,500	0.3
H_2O	36,900	36,900	0.0(1)
S	370	370	0.0(2)
SO_4	920	1,050	14.3(3)
Na	500	500	0.0(4)
Ca	12	12	0.0
Entire Regeneration System			
Total Flows	42,100	43,300	2.8
H_2O	40,400	39,700	-1.7
S	370	550	48.6
SO_4	1,050	1,410	34.3
Na	500	540	8.0
Ca	140	700	400.0

(1) Difference is zero because output includes evaporation which is calculated to give an exact H_2O balance across the scrubber system.

(2) Difference is zero because input includes S absorbed which is calculated to give an exact S balance across the scrubber system.

(3) Serves as an estimate of scrubber oxidation rate.

(4) Difference is zero because the output flow is calculated to give an exact Na balance across the scrubber system.

Table B-5

SUMMARY OF SHORT TERM BALANCES - FEBRUARY 26-28, 1975

	kg/hr		
	Total Input (I)	Total Output (O)	Difference (O - I)/I, %
Scrubber System			
Total Flows	23,400	23,200	-0.8
H_2O	22,300	22,100	-0.9
S	250	246	-1.6
SO_4	570	600	5.3
Na	350	350	0.0(1)
Ca	10.9	10.5	-4.2
Reactor/Clarifier System			
Total Flows	29,100	25,700	-11.9
H_2O	27,800	24,300	-12.5
S	270	260	-3.7
SO_4	670	680	1.5
Na	380	380	0.0
Ca	130	105	-19.2
Filter System			
Total Flows	2,400	2,400	0.0(2)
H_2O	2,010	2,040	1.5
S	61	55	-9.6
SO_4	110	100	-9.1
Na	37	33	-10.8
Ca	90	86	-4.4

(1) Difference is zero because the output flow is calculated to give an exact Na balance across the scrubber system.

(2) Difference is zero because the filtrate flow was estimated to give an exact material balance across the filter system.

The estimated SO_2 absorption was equivalent to 52.7 kg S/hr (116 lb S/hr), the average scrubber evaporation rate was 1930 kg H_2O/hr (4,240 lb/hr), and the average scrubber oxidation rate was equivalent to production of 34 kg of SO_4/hr (74 lb/hr). These figures compare with 60.5 kg S/hr, 6,280 kg H_2O/hr, and 131 kg SO_4/hr in the earlier test. The evaporation estimate for the first intensive test is based on a water balance for the period. That for the second test is based on what is now an apparently inaccurate scrubber outlet temperature because of a buildup around the thermocouple in the stack.

Tables B-6 and B-7 summarize the material balances of two five-day periods of Intensive Test No. 3 (4/26-30/1976 and 5/3-7/1976). The comparable SO_2 removal rates were 95.9 kg S/hr while the water evaporation averaged 6,386 kg H_2O/hr and 6,697 kg H_2O/hr, respectively. Oxidation of sulfur resulted in sulfate formation rates in the scrubber system of 155 kg SO_4/hr (54% of the SO_2 removed) and 162 kg SO_4/hr (54%), respectively.

Table B-6

SUMMARY OF SHORT TERM BALANCES - APRIL 26-30, 1976

	kg/hr		
	Total Input (I)	Total Output (O)	Difference (O - I)/I, %
Scrubber System			
Total Flows	45,600	47,800	4.8
H_2O	42,900	45,200	5.4
S	620	600	-3.2
SO_4	1,540	1,680	9.1
Na	820	820	0.0(1)
Ca	23	22	-4.3
Reactor/Clarifier System			
Total Flows	51,200	49,300	-3.7
H_2O	48,200	46,200	-4.2
S	630	620	-1.6
SO_4	1,770	1,810	2.3
Na	890	880	-1.1
Ca	140	170	21.4
Filter System			
Total Flows	5,160	5,160	0.0(2)
H_2O	4,500	4,490	-0.2
S	105	130	23.8
SO_4	280	310	14.1
Na	61	62	1.6
Ca	154	150	-2.6

(1) Difference is zero because the output flow is calculated to give an exact Na balance across the scrubber system.

(2) Difference is zero because the filtrate flow was estimated to give an exact material balance across the filter system.

Table B-7

SUMMARY OF SHORT TERM BALANCES - MAY 3-7, 1976

	kg/hr		
	Total Input (I)	Total Output (O)	Difference (O - I)/I, %
Scrubber System			
Total Flows	45,500	47,900	5.3
H_2O	42,700	45,100	5.6
S	650	630	-3.1
SO_4	160	177	10.6
Na	865	865	0.0(1)
Ca	19	19	0.0
Reactor/Clarifier System			
Total Flows	50,700	49,900	-1.6
H_2O	47,600	46,300	-2.7
S	680	700	2.9
SO_4	1,900	1,980	4.2
Na	950	940	-1.1
Ca	130	300	131.0
Filter System			
Total Flows	5,820	5,820	0.0(2)
H_2O	4,770	4,990	4.6
S	145	148	2.1
SO_4	375	385	2.7
Na	73	74	1.3
Ca	280	180	-3.6

(1) Difference is zero because the output flow is calculated to give an exact Na balance across the scrubber system.

(2) Difference is zero because the filtrate flow was estimated to give an exact material balance across the filter system.

APPENDIX C

CHEMICAL ANALYSIS PROCEDURES FOR DOUBLE ALKALI PROCESS STREAM SAMPLES

LIST OF PROCEDURES

Method Number	Category	Title
1	Separations	Separation of Solids from Slurries
2		Separation of Solutions Containing Suspended Solids
3		Solids in Filter Cakes
11	Solution Analyses	TOS (Total Oxidizable Sulfur)
12		Sulfate
12a		Total Sulfur
13		Hydroxide
14		Acidity
15		Carbonate
16		Calcium (titrimetric)
16a		Calcium (atomic absorption)
17		Sodium
18		pH
19		Chloride
41	Slurry Analyses	Calcium
42		Hydroxide
51	Solids Analyses	TOS
52		Sulfate
52a		Total Sulfur
53		Hydroxide
54		Carbonate
55		Calcium (titrimetric)
55a		Calcium (atomic absorption)
56		Total Sodium
57		Acid-Insoluble Materials
58		Alkalinity in Lime
59		Calcium in Lime (titrimetric)
60		Carbonate in Lime
62		Carbonate in Soda Ash

SAMPLES

The sample sizes and amounts of reagents are specified for process streams having the following nominal composition:

Solutions: 0.04M TOS, 0.5M sulfate, 0.02M carbonate, 0.02M calcium, 0.1M hydroxide, 0.1M chloride

Solids: calcium (7 millimoles/g), TOS (2 millimoles/g), sulfate (3 millimole/g)

For streams varying significantly from these levels, aliquots and/or reagent volumes should be changed accordingly.

REAGENTS

All of the titrants listed below may be purchased either as prepared solution or as concentrates which are diluted to volume before use. These items can be purchased from many reliable manufacturers. We have used Fisher Scientific and E. Merck reagents.

- 0.1N Iodine solution; should be stored in automatic buret to minimize volatilization losses. Titer should be checked daily versus the 0.1N sodium thiosulfate solution.

- 0.1N Sodium Thiosulfate solution.

- 0.1N Sodium Hydroxide solution, should be stored in automatic buret or plastic reservoir protected from atmospheric carbon dioxide.

- 0.1N Hydrochloric Acid solution

- 0.1M Ethylenediamine tetraacetic Acid (EDTA, disodium salt) solution.

- 0.025M EDTA solution, prepared by volumetric dilution of the 0.1M solution.

- 1M Barium chloride solution, dissolve 210 g of barium chloride crystal in 1000 ml of distilled water.

- 1N Hydrochloric Acid.

- 10% Hydrochloric Acid; mix 1 volume of concentrated Reagent hydrochloric acid with 9 volumes of distilled water. Note: the 1N reagent may be substituted for this.

- 1N Sodium Hydroxide solution, store in automatic buret or plastic reservoir protected from atmospheric carbon dioxide.

- 1M Perchloric acid, prepared by diluting 1 volume of 70-72% (w/w) perchloric acid with 10 volumes of distilled water.

- 0.1M Perchloric acid, prepared by diluting 1 volume of 1M perchloric acid with 9 volumes of distilled water.

- 30% Hydrogen Peroxide solution - Note: we have found that Fisher #H325 and Mallinkrodt #5240 (not stabilized) give low blank values consistently.

- 1N Potassium Hydroxide solution, protected from atmospheric carbon dioxide; solution may be prepared from carbonate-free solids or concentrated stock solution.

- 1M Sodium Perchlorate solution, prepared by dissolving 140 g of $NaClO_4 \cdot H_2O$ in distilled water and diluting to 1 liter with same.

Reagents (continued)

- 0.2000M Sodium Sulfate standard solution, prepared by dissolving 28.41 g of Reagent grade Na_2SO_4 (previously dried at 110° - 120° C for 3 hours) in distilled water and diluting to 1 liter with same.

- 0.1M Lead Perchlorate solution, prepared by dissolving 46.0 g of $Pb(C\ell O_4)_2 \cdot 3H_2O$ (Catalog No. 22118, Alfa Products Division, Ventron Corp., Beverly, Mass.) in CO_2-free distilled water (either boiled or N_2 purged) and diluting to 1 liter with same. This solution should be protected from atmospheric CO_2. Daily standardization of this reagent by titration of a 15-20 mℓ aliquot with the standard Na_2SO_4 solution using the procedure in Method #6 is required both as a check on the free lead concentration and as a confirmation that the electrode system is performing properly.

- 10 mg/ℓ Manganese Chloride solution, prepared by dissolving 0.04 g of $Mn\ C\ell_2 \cdot 4H_2O$ in 1000 mℓ of distilled water.

- 0.015M Mercuric Nitrate solution, prepared by dissolving 5.15 g of $Hg(NO_3)_2\ H_2O$ in 100 mℓ of distilled water containing 0.5 mℓ of concentrated Reagent nitric acid and diluting to 1 liter with distilled water.

- Barium Nitrate solution, saturated; mix approximately 15 g of barium nitrate with 1 liter of distilled water

- Calcium Sulfate. solution, saturated; mix Reagent grade calcium sulfate dihydrate (gypsum) with tap water (room temperature) at the rate of 3 g per liter, mix well and allow solids to settle out before using supernate.

- Acetic acid, glacial, Reagent grade.

- Hydrochloric Acid, concentrated Reagent grade.

- Methyl Alcohol, Reagent grade.

- Phenolphthalein indicator solution, 0.1% in ethanol.

- Thymolphthalein indicator solution, 0.05% in ethanol.

- Bromocresol Green indicator solution, 0.40% in water, neutralized.

- Starch solution, either 5% or 1% in water.

- Calcein indicator solution, 0.02% in water; add potassium hydroxide solution (5N) dropwise to dissolve indicator solids. A 0.1% dry mixture of calcein in KCℓ powder may also be used.

Reagents (continued)

- Methyl red indicator solution, 0.02% in water.

- Cation exchange resin, Dowex 50Wx8, Rexyn 101x8 or equivalent, 20/50 mesh. The resin should be slurried and washed with distilled water to remove all colored species, and the washings checked for the absence of soluble sulfate by adding barium chloride solution to some of the washings. No precipitate or turbidity should be present after a 10-minute reaction time.

- Calcium chloride solution, 2.5 g of $CaCl_2.6H_2O$ in 100 ml distilled water.

- Ammonia Buffer for Magnesium Titrations; mix 6.75 g of ammonium chloride with 57 ml of concentrated Reagent ammonium hydroxide and dilute to 100 ml with distilled water.

- Eriochrome Black T Indicator Solution; 0.5% in ethanol.

SPECIAL APPARATUS

For carrying out the lead titrations for determination of sulfate, the following apparatus is required:

- Lead-Sensitive Specific Ion Electrode, Model 94-82, Orion Research Inc., Cambridge, Mass.
- Double-junction Reference Electrode, with sodium nitrate outer bridge solution so that no chloride or sulfate can flow into the titration solution; Model 90-02 from Orion Research Inc. is recommended.
- pH/millivolt meter, readable to ± millivolt.
- Microburet, 10 mℓ capacity, calibrated at each 0.1 mℓ increment for addition of the 0.2M sodium sulfate titrant.

Note: If available, an automatic titrator or motor-driven buret assembly which can be set up to record the titration curve will be extremely useful.

SAMPLE PREPARATION AND SEPARATION

Note: All solids samples taken from slurries are used as a measure of solids content in the slurry as well as for composition of the solids. The solids sample should be taken from the slurry before the solution sample is order to insure that a representative portion is obtained.

Method #1 - Solids in Slurries

1. Rapidly transfer a 250 mℓ (±2 mℓ) portion of the well-mixed reactor slurry (or 50 mℓ of settler underflow) into a 250 mℓ graduated cylinder. Pour this portion onto a fritted-glass filter crucible (coarse porosity) and start the filtration. The amount of slurry taken may be changed, if necessary, in order to yield at least 2 g of dry solids.

2. Transfer 25 mℓ of wash solution (saturated calcium sulfate solution) into the sample graduate. Just as the liquid level in the filter reaches the top of the solids bed, pour the wash solution onto the solids. In order to avoid possible channeling and inefficient washing, it is extremely important that the liquid level not be allowed to go beneath the surface of the solids.

3. Repeat the displacement wash in Step 2 three times more.

4. Transfer the solids quantitatively to a tared drying dish and dry at 83-85°C to constant weight. This drying step usually requires 3-4 hours in a forced draft oven.

5. Allow the dried solids to cool, then weigh to ± 0.01 g and transfer to a resealable plastic bag for storage. The solids must be ground well prior to analysis.

6. Calculations:

   Reactor Slurries: % Solids (g/100 mℓ) = 0.4 x g of dry solids

   Settler Slurries: % Solids (g/100 mℓ) = 2 x g of dry solids

Method #2 - Solutions Containing Suspended Solids

1. Transfer portions of the slurry into 4 or 6 15 mℓ centrifuge tubes (to give a total volume of 50-60 mℓ) and spin until the supernate is clear. This requires approximately 5 minutes in a small laboratory centrifuge (3600 rpm).

2. Carefully decant the clear supernate into a 60 mℓ polyethylene bottle for storage.

Method #3 - Solids in Filter Cake

1. Dry approximately 20 g (weighed to ± 0.01 g) at 83-85°C to constant weight. This usually requires 3-4 hours in a forced draft oven.

2. Allow the dried solids to cool, then weigh to ± 0.01 g and transfer to a resealable plastic bag for storage. The solids must be ground well prior to analysis.

3. Calculations:

$$\% \text{ Solids} = \frac{\text{g dry solids}}{\text{g wet sample}} \times 100$$

Method #11 - Total Oxidizable Sulfur (TOS)

1. Transfer 25 mℓ (measured to ±.02 mℓ) of 0.1 I_2 solution into a 125 mℓ Erlenmeyer flask and cover with a watchglass.

   Note: Experience may show that some sample streams require less iodine.

2. Add approximately 20 mℓ of distilled water and 2 mℓ of glacial acetic acid. In lieu of acetic acid, 15 mℓ of 0.1N HCℓ may be used.

3. Pipet 10 mℓ of sample (volumetric pipet) directly into the acidified iodine solution while swirling the solution to assure rapid mixing of the sample. If all iodine color is discharged, repeat the procedure using more I_2 sclution and adjust calculations accordingly.

4. Back titrate with 0.1$\underline{N}$ $Na_2S_2O_3$ to pale yellow color. Add starch solution to give blue color and continue dropwise addition of titrant to disappearance of blue color.

5. Calculations:

$$\text{TOS (moles/ℓ)} = \frac{[(\text{mℓ } I_2)(\underline{N}\ I_2)]-[(\text{mℓ } S_2O_3)\ (\underline{N}\ S_2O_3)]}{(2)\ (10\ \text{mℓ})}$$

where: $\underline{N}$ I_2 is the normalty of the I_2 solution

$\underline{N}$ S_2O_3 is the normality of the $Na_2S_2O_3$ solution

2 is the equivalence factor for moles of oxidizable sulfur

Method #12 - Sulfate

Note: If only an approximate value for sulfate is needed for samples containing low TOS and carbonate, the determination may be carried using the sample aliquot plus 60 mℓ of distilled water starting with Step 5.

1. Set up sparging/boiling apparatus as shown in Figure C-1 and add 30 mℓ of distilled water and 10 mℓ of 1M perchloric acid to the Erlenmeyer flask(s).

2. Heat the solution nearly to boiling and purge with a gentle nitrogen flow for 3 minutes to remove dissolved oxygen. Allow to cool slightly.

3. Pipet a 2 mℓ aliquot of sample into the flask.

4. Heat to boiling and purge with N_2 for 15 minutes. Note: A Pasteur pipet or bubbler tube may be substituted for the gas dispersion tube in which case, the N_2 purge should be continued for 30 minutes.

5. Allow to cool and transfer purged solution into a 150 mℓ beaker. Add 2 drops bromocresol green indicator solution and neutralize solution with 1N NaOH adding one drop of 1M $HC\ell O_4$ after indicator has turned green.

6. Add 10 mℓ of 1M $NaC\ell O_4$ solution and enough methanol to make a 50% (v/v) solution.

7. Under rapid stirring, add 25 mℓ of standardized (0.1M) lead perchlorate solution. The amount of lead added should be such that an excess of lead remains in solution. If necessary readjust pH of solution to 3.5-4.5 with $HC\ell O_4$ or NaOH.

8. Back titrate the excess lead with 0.2M Na_2SO_4 solution using the EMF between the lead-selective specific ion electrode and the double-junction reference electrode to indicate the endpoint. Titrant increments at the endpoint should be 0.1 mℓ. The endpoint region can be seen from the daily standardization curve, and may vary due to changes in the condition of the lead electrode. The endpoint can be determined graphically or by means of the second derivative technique.

9. Calculations:

$$\text{Sulfate (moles/}\ell\text{)} = \frac{[(\text{m}\ell \text{ lead perchl.})(\text{M lead perchl.})] - [(\text{m}\ell\ Na_2SO_4)(\text{M } Na_2SO_4)]}{\text{m}\ell \text{ of sample}}$$

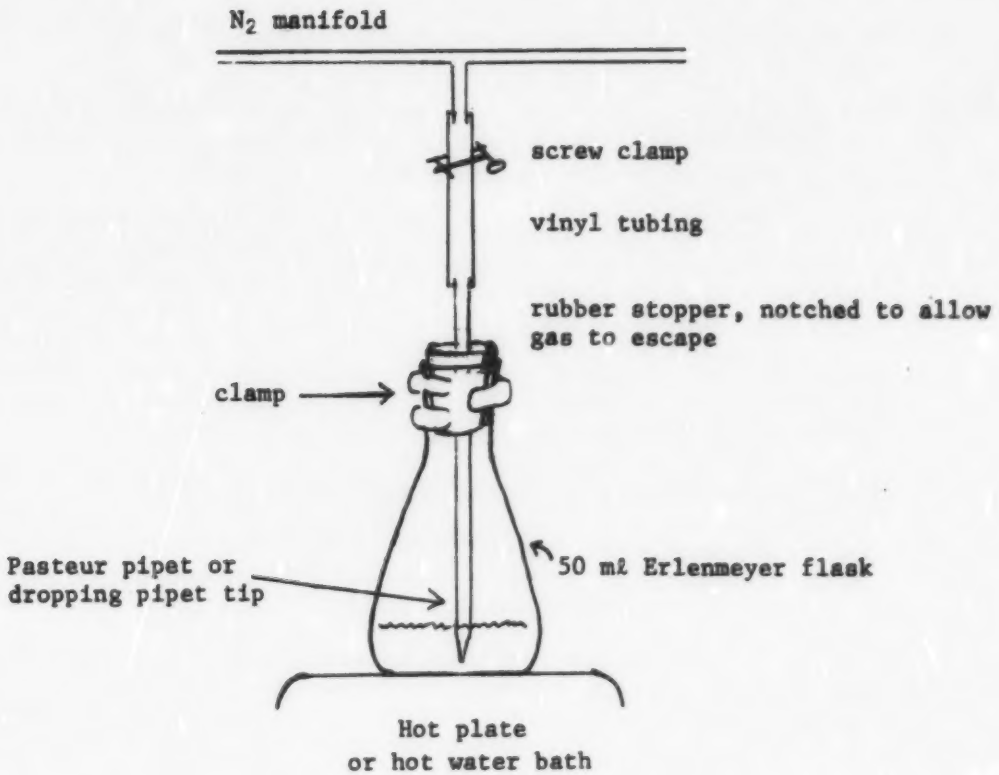

Figure C-1

APPARATUS FOR SULFATE DETERMINATION

Method #12a - Total Sulfur (Gravimetric)

1. Transfer 2 mℓ of 1N NaOH into a 100 mℓ beaker, and add approximately 10 mℓ of distilled H_2O and a drop of phenolphthalein solution.

2. Pipet a 2 mℓ aliquot of sample into the NaOH solution. If necessary, add more NaOH to give a pink color to solution.

3. Add (graduated cylinder or pipet) 5 mℓ of 30% hydrogen peroxide solution. Swirl to mix, cover beaker and allow to stand for 15 minutes.

4. Transfer to a 400 mℓ beaker and dilute to approximately 250 mℓ with distilled water.

5. Add 10% HCℓ dropwise until disappearance of the pink color. Then add 3-4 drops of methyl red indicator and continue dropwise addition of 10% HCℓ until the solution turns red.

6. Heat on hot plate nearly to boiling, and then add 25 mℓ of 1M barium chloride solution while stirring the solution rapidly. Make certain that the solution is still acid (red) to methyl red indicator.

7. Allow precipitate to settle and test for completeness of precipitation with a few drops of the barium chloride solution. If necessary add more barium chloride solution in 5 mℓ increments, testing for completeness of precipitation after each addition.

8. Digest sample hot (below boil) for at least 3 hours.

9. Gravity filter the hot solution and precipitate through Whatman #42 (or equivalent) filter paper. Use a rubber policeman to effect quantitative transfer of precipitate.

10. Test for completeness of washing by adding a drop of 0.1N silver nitrate solution to a few drops of wash liquor from the tip of the funnel stem. If only a very faint turbidity appears, washing is complete.

11. Transfer the filter paper and precipitate into a preignited crucible. Place in a cold muffle furnace and ignite at 850°C for three hours.

12. Cool crucible in dessicator and weigh.

13. Calculations:

$$\text{Total S (moles/ℓ)} = \frac{(\text{g } BaSO_4)}{(2 \text{ mℓ})(0.2334)}$$

where: 0.2334 is the millimolecular weight (g/millimole) of $BaSO_4$

Method #13 - Hydroxide

1. Pipet a 10 mℓ aliquot of sample into a 125 mℓ Erlenmeyer flask. Add approximately 25 mℓ of distilled water, 10 mℓ of 2.5% calcium chloride solution, and 2-3 drops of thymolphthalein.

2. Titrate with o.1N HCℓ to the disappearance of the blue color. Note: if too much indicator has been added, the endpoint is seen as a marked decrease in the intensity of the blue color, rather than complete disappearance.

3. Calculations:

$$\text{Hydroxide (moles/ℓ)} = \frac{(\text{mℓ HCℓ})\ (\underline{\text{N}}\ \text{HCℓ})}{10}$$

Method #14 - Acidity

1. Transfer 15 mℓ (± .01mℓ) of 0.1N NaOH solution into a 125 mℓ Erlenmeyer flask, and add 2-3 drops of thymolphthalein indicator solution.

2. Pipet a 10 mℓ aliquot of sample into the NaOH solution and mix well.

3. If solution remains blue, titrate with 0.1N HCℓ to disappearance of blue. Note: If too much indicator has been added, the endpoint is seen as a marked decrease in intensity of the blue color when 1-2 drops of HCℓ are added.

4. If indicator color disappears during addition of sample and does not reappear upon mixing, repeat the determination using a larger aliquot of 0.1N NaOH.

5. The exact N of the NaOH is determined by titrating a known volume (15mℓ, ±.01 mℓ) with 0.1N HCℓ to the thymolphthalein endpoint. Then

$$\underline{\text{N}}\ \text{NaOH} = \frac{\text{mℓ HCℓ}}{\text{mℓ NaOH}} \times (\underline{\text{N}}\ \text{of HCℓ})$$

6. Calculations:

$$\text{Acidity (moles/ℓ)} = \frac{[\ (\text{mℓ NaOH})\ (\underline{\text{N}}\ \text{NaOH})\ ] - [(\text{mℓ HCℓ})(\underline{\text{N}}\ \text{HCℓ})\ ]}{10\ \text{mℓ}}$$

where: N NaOH - the exact normality determined above.

Method #15 - Carbonate

Note: Once the determination is started, it must be carried through Step 7 (acid to bromocresol green) in order to avoid error from absorption of atmospheric CO_2.

1. Transfer 25 mℓ of 0.1N NaOH into a 125 mℓ Erlenmeyer flask and add 1 drop of phenolphthalein indicator solution.

2. Pipet a 10 mℓ aliquot of sample solution into the sodium hydroxide.

3. If the phenolphthalein color disappears immediately, add an additional 10 mℓ of NaOH solution. The pink (alkaline) indicator color should persist for at least 30 seconds.

4. Add 5 mℓ of 30% hydrogen peroxide, mix well and allow to stand for 10 minutes. Add 1 mℓ of the 10 mg/liter manganese solution, and boil until effervescence ceases.

5. Cool quickly in water bath. If pink color has faded, add 1 drop of the phenolphthalein solution to ascertain that solution is still alkaline.

6. Titrate with 0.1N HCℓ to disappearance of pink color. Note: If too much indicator has been added, the endpoint is seen as a marked decrease in intensity of the red color. Note the volume (level) of 0.1N HCℓ in the buret, and call this "A".

7. Add 3-4 drops of bromocresol green indicator solution to the titration solution, and continue titration with 0.1N HCℓ until a permanent yellow color is seen. Then add 3 mℓ of titrant in excess. Note the reading of the HCℓ buret and call this "B".

8. Quantitatively transfer the titrated solution to a 150 mℓ beaker and boil (uncovered) for 10 minutes. Note: It may be necessary to add small amounts of distilled water during the boiling in order to avoid spattering losses.

9. Cool the solution, and back-titrate with 0.1N NaOH to a green endpoint. Call this volume "C".

10. Run at least one blank determination on all reagents.

11. Calculations:

$$\text{Millimoles carbonate} = [(B-A) \times N\ HC\ell] - [C \times N\ NaOH]$$

$$\text{Carbonate (moles/}\ell) = \frac{(\text{millimoles } CO_3 \text{ in sample}) - (\text{millimoles } CO_3 \text{ in blank})}{10\ m\ell}$$

where: N HCℓ = normality of HCℓ

N NaOH = normality of NaOH to bromocresol green

Method #16 - Calcium via EDTA Titration

1. Pipet a 25 mℓ aliquot of sample into a 250 mℓ Erlenmeyer flask, and add 35 mℓ distilled water.

2. Add 10 mℓ of 10% HCℓ and mix well. Then either boil or sparge with nitrogen gas for 10 minutes.

3. Add 0.1N I_2 solution until an excess (permanent pale yellow color) is present. Then add 0.1N $Na_2S_2O_3$ solution dropwise until the yellow color is just discharged. Avoid adding an excess of $Na_2S_2O_3$.

4. Add 15 mℓ of 1N KOH followed by 15 mℓ of 1% KCN. Note: The potassium hydroxide must be added before the cyanide solution.

5. Add a small amount of the calcein indicator (either 1-2 drops of solution or a few milligrams of dry mixture) sufficient to give a visible green fluorescence. Illumination with longwave (360 nm) ultraviolet light will greatly enhance the fluorescence. As with most most indicators, the amount added should be only the minimum necessary to observe the fluorescence. A large excess of indicator will result in a poorly defined endpoint.

6. Titrate with 0.025M EDTA solution to the disappearance of the fluorescence. If a large amount of calcium is present, the fluorescence may reappear after a few seconds due to dissolution of precipitated calcium hydroxide. The true endpoint is stable for at least 2 minutes. Note: Use of an ultraviolet light allows this indicator to be used for extremely turbid solutions, if necessary.

7. Calculations:

$$\text{Calcium (moles/ℓ)} = \frac{(\text{mℓ EDTA})\ (\text{M EDTA})}{25}$$

Method #16a - Calcium via Atomic Absorption Spectrometry

Note: This method can be used as the routine method if the analyst has easy access to an AA spectrometer. The details of operation of the instrument are found in the instruction manual for that instrument.

1. Dilute a 5 mℓ aliquot to 250 mℓ with distilled water. Call this Solution I.

2. Dilute a 5 mℓ aliquot of Solution I to 50 mℓ with distilled Water. Call this Solution II.

3. Dilute 5 mℓ of Solution II plus 1 mℓ of 1% $LaCl_3$ (in 2.5% HCl) to 10 mℓ with distilled water. Call this Solution III.

3. Calcium calibration standards should be prepared (including the lanthanum solution) and run in order to bracket the sample concentration. The usual range for the measured solution is from 0-10 milligrams of calcium/liter.

4. Measure the absorbances of Solution II and of standards on the atomic absorption spectrometer at the most sensitive calcium wavelength of 422.7 nanometers.

5. Determine the calcium concentration (in milligrams/ℓ) in Solution II from the calibration data.

6. Calculations:

$$\text{Calcium (milligram/ℓ)} = D \times \frac{250}{5} \times \frac{50}{5} \times \frac{10}{5} = D \times 100$$

$$\text{Calcium (mole/ℓ)} = \frac{D}{(40.1)(1000)} \times \frac{10}{5} \times \frac{250}{5} \times \frac{50}{5} = \frac{D}{40}$$

where: D is the concentration (milligram/ℓ) of calcium in Solution II,

40 is the atomic weight (gram/mole) of calcium

Method #17 - Sodium via Atomic Absorption Spectrometry

Note: (a) All glassware used in these measurements must be cleaned in dilute (4M) nitric or hydrochloric acid before use in order to minimize sodium contamination.

(b) In order to lessen the effect of contamination with extraneous sodium, the measurements are made at 330 nanometers, a relatively insensitive line.

(c) The operational details of the particular instrument are found in the instrument instructional manual.

1. Dilute a 5 mℓ aliquot of sample to 100 mℓ with distilled water. Call this Solution I.

2. Dilute 10 mℓ of Solution I to 100 mℓ with distilled water. Call this Solution II.

3. Prepare appropriate sodium calibration standards in distilled water. The usual range if from 0-200 milligrams of sodium/liter.

4. Measure the absorbances of Solution II and of the standards on the atomic absorption spectrometer at the 330 nanometer (secondary) sodium line.

5. Determine the sodium concentration in Solution II from the calibration data.

6. Calculations:

$$\text{Sodium (moles/)} = \frac{E}{(23)(1000)} \times \frac{100}{5} \times \frac{100}{10} = \frac{E}{115}$$

where: E is the concentration (milligram/ℓ) of sodium in Solution II,

23 is the atomic weight (gram/mole) of sodium

Method #18 - Measurement of pH .

The pH can be measured with any glass-reference electrode set provided that the following points are observed:

1. The glass electrode must be clean and free of cracks and other marks. A wide range (0-14 pH) industrial-quality electrode is best. A new glass electrode should be soaked in water (or pH4 buffer solution) for 1/2 hour before use.

2. The reference electrode must be filled with the appropriate electrolyte. Electrical conductivity through the liquid junction must be confirmed. A sleeve-type junction is best for this purpose, although the electrolyte level must be checked frequently since the electrolyte leakage rate tends to be high with this junction.

3. The electrode pair must be set (i.e. standardized) using a standard buffer reasonably near the expected sample pH, and cross-checked against a buffer beyond the expected sample pH. This latter check is extremely important to prove the linearity of electrode response in the region of interest. Provided that fresh buffers are used, the indicated pH should be within 0.1 pH unit for the check (second) buffer.

Method #19 - Chloride

1. Pipet a 10 mℓ aliquot of sample into a 125 mℓ Erlenmeyer flask.

2. Add 10 mℓ of distilled water, 2 drops of phenolphthalein indicator solution and sufficient 1N NaOH to give a red color.

3. Add 2 mℓ 30% H_2O_2, mix and let stand for 10 minutes.

4. Add 1 mℓ of the 10 mg/ℓ solution of manganese. (The amount of chloride added is neglible, equivalent to only 4×10^{-5}M chloride in the sample.)

5. Heat solution to boiling for approximately 15 minutes to destroy the peroxide, adding more distilled water if necessary to maintain liquid level. Note: Absence of peroxide is indicated by change in the boiling (gas evolution) character, or by failure to bleach the color when another drop of indicator is added to the solution.

6. Cool the solution to room temperature, add 3-4 drops of bromocresol green indicator and bring just to the green color with 1M perchloric acid ($HC\ell O_4$). Then make yellow-green with 0.1M perchloric acid (and 0.1N NaOH, if necessary).

7. With rapid swirling, add 20 mℓ of saturated $Ba(NO_3)_2$ solution and sufficient bromocresol green indicator to see the color. Add 0.1M perchloric acid and 0.1N NaOH to achieve a yellow-green color.

8. Add 10 drops diphenylcarbazone indicator solution and titrate with 0.015M $Hg(NO_3)_2$ solution to a faint purple endpoint which is stable for at least 30 seconds.

9. Calculations:

$$\text{Chloride (moles/ℓ)} = \frac{(\text{mℓ Hg Titrant})(\text{M of titrant})(2)}{10\ \text{mℓ}}$$

10. Standardization of $Hg(NO_3)_2$ Titrant: Titrate a 2 mℓ aliquot of 0.1N HCℓ using the procedure outlined above.

$$\text{M of titrant} = \frac{(2\ \text{mℓ})(\text{N HC}\ell)}{(\text{mℓ titrant})(2)}$$

Method #41 - Calcium In Lime and Limestone Slurries

Note: Sample aliquot should be weighed if analyses are to be expressed as weight percent. The method is set up for 10% (w/v) slurries; sample size and/or dilution may have to be modified for other concentration.

1. Pipet a 10 mℓ aliquot of well-mixed slurry into a 250 mℓ beaker. Add 50 mℓ distilled water and 1-2 drops of phenolphthalein solution.

2. Add sufficient 10% HCℓ to neutralize the alkalinity. Then add 10 mℓ more of 10% HCℓ for lime slurries, or 25 mℓ more of 10% HCℓ for limestone slurries. Warm the solution, if necessary, to dissolve all solids (some silica may remain undissolved).

3. Dilute to 250 mℓ in a volumetric flask with distilled water.

4. Pipet a 25 mℓ aliquot into a 100 mℓ beaker, and boil for 15 minutes adding distilled water to maintain liquid level.

5. Continue titration as in Method #16 using 0.1M EDTA titrant.

6. Calculations:

$$\text{Calcium (mole/ℓ)} = \frac{(\text{mℓ EDTA})(\text{M of EDTA})}{10\ \text{mℓ}} \times \frac{250}{25}$$

Method #42 - Hydroxide (in lime slurries)

Note: The method is set up for a 10% (w/v) slurry. Sample size should be varied appropriately for other concentrations.

1. Pipet a 5 mℓ aliquot of well-mixed slurry into a 250 mℓ Erlenmeyer flask. Add 100 mℓ of distilled water and 2-3 drops of phenolphthalein solution.

2. Titrate with 1N HCℓ to the disappearance of the pink color.

3. Calculation:

$$Ca(OH)_2\text{(mole/ℓ)} = \frac{(\text{mℓ HCℓ})(\text{N HCℓ})}{(5\ \text{mℓ})(2)}$$

Solids Analyses

Note: Solids analyses are always carried out on dried, ground solids unless otherwise noted.

Method #51 - Total Oxidizable Sulfur (TOS) (Iodine Titration)

1. Weigh out from 0.18 g to 0.2 g (weighed to ±0.0001 g) of solids on a weighing paper or boat.

2. Transfer 25.00 mℓ of 0.1N I_2 solution into a 250 mℓ Erlenmeyer flask. Add approximately 75 mℓ of distilled water and 10 mℓ of 10% HCℓ.

3. Quickly transfer the weighed solids to the iodine solution and cover the flask with a watchglass.

4. Stir the suspension until all of the solids have dissolved. A magnetic stirrer is useful for this operation. Break up any lumps with a glass rod. Note: In solids with a very high $CaSO_4$ content, not all of the solids will dissolve in the acid. In general all solids should dissolve in 30 minutes.

5. As soon as all solids have dissolved, back titrate the excess I_2 with 0.1N $Na_2S_2O_3$. When the solution has reached a pale yellow color, add starch solution to give a blue color. Continue the titration dropwise until the blue color is discharged.

6. Carry at least one reagent blank through the process, using the same length of stirring time as for the sample. This will help to ascertain whether air oxidation is causing an interference in the method. The blank titer (mℓ $Na_2S_2O_3$ per mℓ of I_2 taken) should be within 0.005 of the standardization titer.

7. Calculations:

$$\text{TOS (millimoles/g)} = \frac{(\text{mℓ } I_2 \times \underline{N}\ I_2) - (\text{mℓ } S_2O_3 \times \underline{N}\ S_2O_3)}{(2)(\text{g sample})}$$

where: $\underline{N}\ I_2$ and $\underline{N}\ S_2O_3$ are the normalities of the I_2 and $Na_2S_2O_3$ solutions.

2 is the equivalence factor for moles of oxidizable sulfur.

Method #52 - Sulfate In Solids

1. Set up the sparging/boiling apparatus as shown in Figure A-1, and add 30 mℓ of distilled water to the Erlenmeyer flask(s).

2. Heat the water to boiling and purge with a gentle nitrogen flow for 3 minutes to remove dissolved oxygen.

3. Transfer 0.2 g to 0.3 g (weighed to ±0.0001 g) of sample to the purged water.

4. Purge with nitrogen for 3 minutes more, then quickly add 10 mℓ of 1M perchloric acid (restopper flask quickly) to dissolve sample.

5. When all solids have dissolved, bring to a boil and purge for at least 30 minutes (no less). Then cool solution.

6. Transfer the solution to a 150 mℓ beaker, add 2 drops bromocresol green indicator and neutralize (to within 1 drop on the acid, yellow, side) with 1M NaOH and 1M $HC\ell O_4$.

7. Add 5 grams of washed cation exchange resin, and mix (magnetic stirrer) for 30 minutes.

8. Filter the solution and resin through a one (1) inch thick bed of the same resin contained in a sintered glass filter crucible, and wash through with distilled water. The total volume of solution plus washes should be less than 100 mℓ. Note: This ion-exchange operation can also be carried out on a column containing 10 gm of resin.

9. Allow to cool and transfer purged solution into a 150 mℓ beaker. Add 2 drops bromocresol green indicator solution and neturalize solution with 1N NaOH adding one drop of $HC\ell O_4$ after indicator has turned green.

10. Add 10 mℓ of 1M $NaC\ell O_4$ solution and enough methanol to make a 50% (v/v) solution.

11. Under rapid stirring, add 25 mℓ of standardized (0.1M) lead perchlorate solution. The amount of lead added should be such that an excess of lead remains in solution. If necessary readjust pH of solution to 3.5-4.5 with $HC\ell O_4$ or NaOH.

12. Back titrate the excess lead with 0.2M Na_2SO_4 solution using the EMF between the lead-selective specific ion electrode and the double-junction reference electrode to indicate the endpoint. Titrant increments at the endpoint should be 0.1 mℓ. The endpoint region can be seen from the daily standardization curve, and may vary due to changes in the condition of the lead electrode. The endpoint can be determined graphically or by means of the second derivative technique.

13. Calculations:

Sulfate (millimoles/g) =

$$\frac{[(\text{ml lead perchl.})(\underline{M}\text{ lead perchl.})] - [(\text{ml } Na_2SO_4)(\underline{M}\ Na_2SO_4)]}{\text{g sample}}$$

Method #52a - Total Sulfur (gravimetric)

1. Weigh out from 0.13 g to 0.15 g (weighed to ± 0.0001 g) of solids and transfer them into a 150 ml beaker. Add 25 to 50 ml of distilled water and 1 drop of phenolphthalein indicator solution.

2. While stirring the suspension, add 0.1N NaOH dropwise until a permanent pink color is achieved.

3. Add 5 ml of 30% hydrogen peroxide solution, mix well and allow to stand for 15 minutes.

4. With constant stirring add 0.1N HCl dropwise until the pink of phenolphthalein disappears. Then add 2-3 drops of methyl red indicator solution.

5. Continue the stirring and the dropwise addition of 0.1N HCl until the solution turns red. Then add a few drops more of the 0.1N HCl slowly.

6. If solids do not dissolve after 10 minutes, add a few drops more of the 0.1N HCl. Continue stirring until all solids have dissolved.

7. Add 2 g of the washed ion exchange beads, and allow the beads to remain in the solution for 1 hour with frequent stirring.

8. Decant as much liquor as possible into a 400 ml beaker, and filter off the beads on a sintered glass Buchner funnel. Wash the beaker and beads with distilled water, and add the washings to the decanted liquor.

9. Dilute the solution to 250 ml with distilled water, and carry out the precipitation and ignition as in Method #6a, starting with Step 6.

10. Calculations:

$$\text{Total Sulfur (millimoles/g)} = \frac{\text{g } BaSO_4}{(\text{g sample})(0.2334)}$$

where: 0.2334 is the millimolecular weight (g/millimole) of $BaSO_4$

Method #53 - Hydroxide

1. Weigh out from 0.50 g to 0.55 g (weighed to ±0.0001 g) of sample and transfer to a 125 mℓ Erlenmeyer flask containing 40 mℓ of distilled water and magnetic stirring bar.

2. Add 2-3 drops of thymolphthalein indicator solution and 10 mℓ of 2.5% calcium chloride solution.

3. Titrate with 0.1N HCℓ to the disappearance of the blue color. The indicator color may reappear on continued stirring. The titration should be continued until the endpoint holds for at least one minute. Note: If too much indicator has been added the endpoint is seen as a marked decrease in the intensity of the blue color.

4. Calculations:

$$\text{Hydroxide (millimoles/gram)} = \frac{(\text{mℓ HCℓ})(\underline{\text{N}}\ \text{HCℓ})}{\text{g sample}}$$

Method #54 - Carbonate

Because calcium is present in the solids, the carbonate is separated and measured as CO_2 after first oxidizing all sulfite species to sulfate. Note: Once the determination is started, it must be carried through Step 13 (acid to bromocresol green) in order to avoid error from absorption of atmospheric CO_2.

1. Set up the apparatus shown schematically in Figure C-2. Three midget impingers or midget bubblers in series will give a 98% collection efficiency for CO_2.

2. Just prior to performing the analysis, place 50 mℓ of 0.1N HCℓ and 3 mℓ of methyl red indicator solution into the addition funnel. Also transfer 15 mℓ of 0.5N NaOH into each of the midget impingers.

3. Transfer between 1.0 g and 1.1 g (weighed to ±0.0001 g) of the solids into the reactor, and add a magnetic stirring bar, and 50 mℓ of distilled water.

4. Add 1 drop of phenolphthalein solution, and then add 0.1N NaOH dropwise until a permanent faint pink color is seen in solution.

5. Add 5 mℓ of 30% hydrogen peroxide and immediately seal the system. Then start the magnetic stirrer.

6. Start the sparging system and adjust to give an air flow of approximately 2 liters/minute.

7. Add the 0.1N HCℓ slowly into the reactor until the yellow color (from the methyl red) turns red.

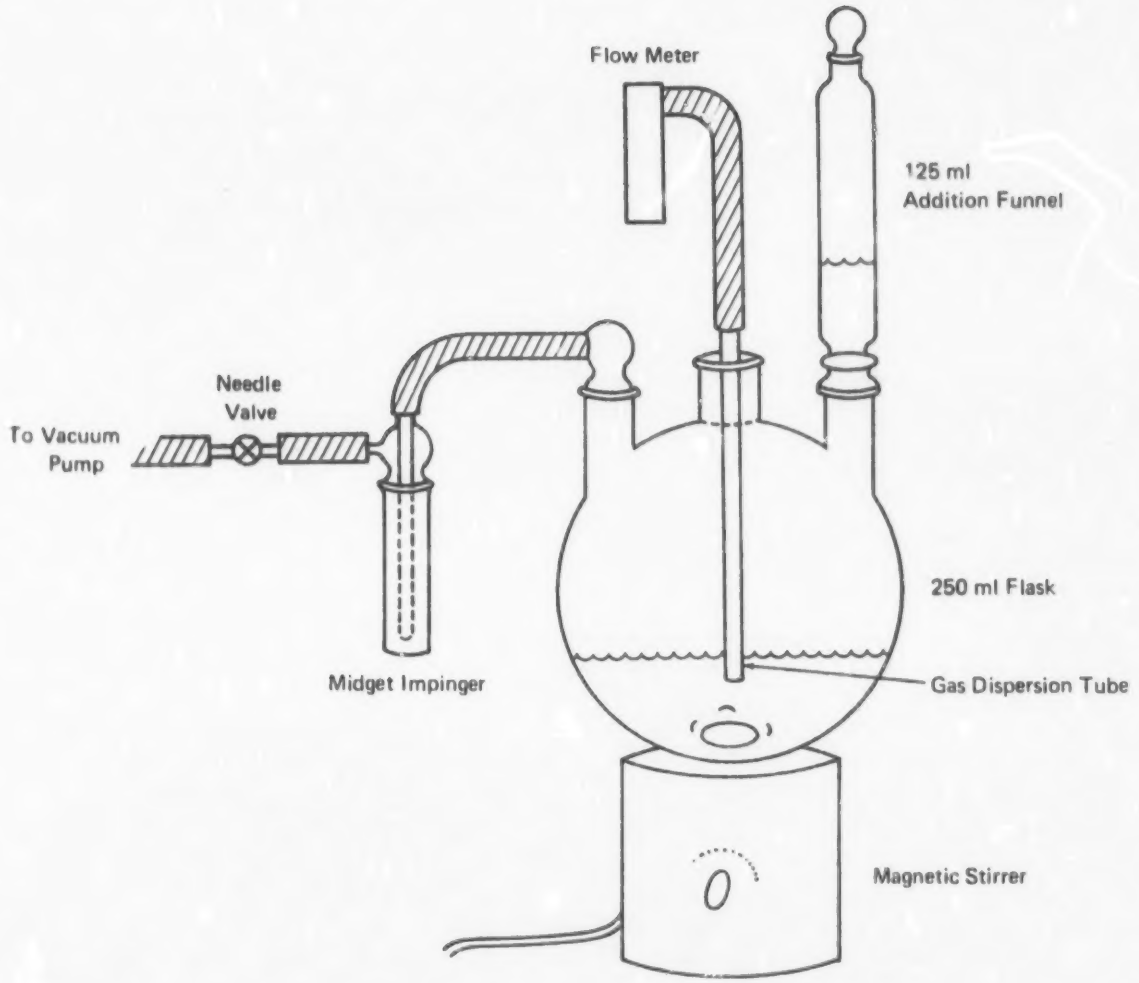

Figure C-2

APPARATUS FOR CARBONATE IN SOLIDS

8. Continue stirring and sparging until all the solids dissolve. It may be necessary to add more the of 0.1N HCℓ dropwise in order to achieve complete solution.

9. Once all solids have dissolved, continue the purge for 15 minutes more.

10. Transfer the impinger solutions to a 150 mℓ beaker washing the impinger with distilled water to effect quantitative transfer.

11. Add 1 mℓ of 30% H_2O_2, mix and let stand 15 minutes (covered).

12. Add 1 mℓ of the 10 mg/liter manganese solution and boil the solution (covered with a watchglass) for 5 minutes. Cool the solution to near room temperature quickly (to minimize exposure to atmospheric CO_2).

13. Add to the impinger solution, 1 drop of phenolphthalein solution and 5 mℓ (pipet) of 1N HCℓ.

14. Titrate with 0.1N HCℓ to disappearance of pink color. Note: if too much indicator has been added, the endpoint is seen as a marked decrease in intensity of the red color. Note the volume (level) of 0.1N HC in the buret, and call this "A".

15. Add 3-4 drops of bromocresol green indicator solution to the titration solution, and continue titration with 0.1N HCℓ until a permanent yellow color is seen. Then add 3 mℓ of titrant in excess. Note the reading of the HCℓ buret and call this "B".

16. Quantitatively transfer the titrated solution to a 150 mℓ beaker and boil (uncovered) for 10 minutes. Note: It may be necessary to add small amounts of distilled water during the boiling in order to avoid spattering losses.

17. Cool the solution and back-titrate with 0.1N NaOH to a green endpoint. Call this volume "C".

18. Run at least one blank determination including sparging for the same amount of time.

19. Calculations:

Millimoles carbonate - [(B-A) x N HCℓ] - [C x N NaOH]

Carbonate (millimoles/gram =

$$\frac{(\text{millimoles } CO_3 \text{ in sample}) - (\text{millimoles } CO_3 \text{ in blank})}{\text{g sample}}$$

where: N HCℓ = normality of HCℓ

N NaOH = normality of NaOH to bromocresol green

Method #55 - Calcium (titrimetric)

1. Weigh out 0.13 g to 0.14 g (weighed to ± 0.0001 g) of sample and transfer into a 250 mℓ beaker.

2. Add 10-15 mℓ of distilled water and 5 mℓ of 10% HCℓ, and mix well to dissolve solids. Then add 60 mℓ more of distilled water.

3. Boil or purge with nitrogen gas for 10 minutes.

4. Add 0.1N I_2 solution until an excess (yellow color) is present. Then add 0.1N $Na_2S_2O_3$ solution dropwise until the yellow color is just discharged. Avoid adding an excess of $Na_2S_2O_3$.

5. Add 15 mℓ of 1N KOH followed by 15 mℓ of 1% KCN. Note: The potassium hydroxide must be added before the cyanide solution.

6. Add a small amount of the calcein indicator (either 1-2 drops of solution or a few milligrams of dry mixture) sufficient to give a visible green fluorescence. Illumination with longwave (360 nm) ultraviolet light will greatly enhance the fluorescence. As with most indicators, the amount added should be only the minimum necessary to observe the fluorescence. A large excess of indicator will result in a poorly defined endpoint.

7. Titrate with 0.1M EDTA solution to the disappearance of the fluorescence. If a large amount of calcium is present, the fluorescence may reappear after a few seconds due to dissolution of precipitated calcium hydroxide. The true endpoint is stable for at least 2 minutes. Note: Use of an ultraviolet light allows this indicator to be used for extremely turbid solutions, if necessary.

8. Calculations:

$$\text{Ca (millimoles/g)} = \frac{(\text{mℓ EDTA}) \times (\text{M EDTA})}{\text{g sample}}$$

Method #55a - Calcium (Atomic Absorption Spectrometry)

Note: This method can be used when the analyst has easy access to an AA spectrometer. The details of operation of the instrument can be found in the particular instrument manual.

1. Weigh out 0.10 g to 0.11 g (weighed to 0.0001 g) of sample, transfer into a 150 mℓ beaker and add 25 mℓ of 10% HCℓ.

2. Stir to dissolve all solids and then dilute to 250 mℓ in a volumetric flask with distilled water. Call this Solution I.

3. Mix 5 mℓ of Solution I with 5 mℓ of 1% $LaCℓ_3$ (in 2.5% HCℓ) and dilute to 50 mℓ with distilled water. Call this Solution II.

4. Calcium standards should be prepared (including the lanthanum solution) and measured in order to bracket the sample concentration. The usual range in the measured solution is from 0-10 milligrams of calcium per liter.

5. Measure the absorbances of Solution II and of the standards on the atomic absorption spectrometer at the most sensitive calcium wavelength, 422.7 nanometers. Either an air/acetylene or a nitrous oxide flame may be used, although the latter gives a more linear calibration.

6. Determine the calcium concentration (in milligrams/liter) in Solution II from the calibration data.

7. Calculations:

Calcium (millimoles/g) =

$$\frac{E}{\left(\frac{\text{g sample}}{250\ \text{m}}\right)\ (0.040)(100\ \text{mg/g})(1000\ \text{mℓ/ℓ})\ \left(\frac{5}{50}\right)}$$

$$= \frac{E(0.0625)}{(\text{g sample})}$$

where: 0.040 is the milliatomic weight (g per millimole) of calcium
E is the measured calcium concentration (mg/ℓ)

Method #56 - Total Sodium

Notes: (a) All glassware used in these measurements must be cleaned in dilute (3 or 4 M) nitric or hydrochloric acid before use in order to minimize sodium contamination.

(b) In order to lessen the effect of contamination with extraneous sodium, the measurements are made at 330 nanometers, a relatively insensitive line.

(c) Operational details of the particular instrument are found in the instrument instruction manual.

1. Weigh out 1.0 g to 1.2 g (weighed to ± 0.001 g) of sample and dissolve in 25 mℓ of 10% HCℓ plus approximately 100 mℓ of distilled water. Then dilute to 250 mℓ with distilled water.

2. Prepare appropriate sodium calibration standards in distilled water. The usual range is from 0-200 milligrams of sodium/liter.

3. Measure the absorbances of the diluted sample and of the standards on the atomic absorption spectrometer at the 330 nanometer sodium line.

4. Determine the sodium concentration (C) in the sample solution from the calibration data.

5. Calculations:

$$\text{Total Sodium (weight percent)} = \left(\frac{C}{\text{g sample}}\right)\left(\frac{250}{1000}\right)\left(\frac{1}{1000}\right)\left(100\right)$$

where: C is the concentration (milligram/liter) of sodium in the diluted sample

$$\text{Total Sodium (millimoles/g)} = \left(\frac{C}{\text{g sample}}\right)\left(\frac{250}{1000}\right)\left(\frac{1}{0.0230}\right)\left(\frac{1}{1000}\right)$$

where: C is the concentration of sodium in the measured solution

0.0230 is the milliatomic weight (g/millimole) of sodium

Method #57 - Magnesium (titrimetric)

Note: This test is an empirical test designed to provide an estimate of insoluble materials (principally silicates) coming both from the lime and from the flyash.

1. Transfer between 3 g and 7 g (weighed to $\pm$ 0.001 g) of ground sample into a 250 mℓ beaker.

2. Add 100 mℓ of 10% HCl, and stir for 30 minutes.

3. Filter through a medium porosity sintered glass filter funnel that has been previously dried and tared under the same conditions as used for the sample.

4. Wash the acid-insolubles with 50 mℓ of distilled water.

5. Dry to constant weight (2-3 hours) at 105° - 110° C and obtain (net) weight of dried acid-insolubles.

6. Calculations:

$$\text{Weight Percent Acid Insolubles} = \frac{\text{g dry insolubles}}{\text{g sample}} \times 100$$

Method #58 - Available Alkalinity in Lime

1. Weigh out between 0.3 g and 0.35 g (weighed to 0.0001 g) of well-mixed sample and transfer to an Erlenmeyer flask containing approximately 100 mℓ of distilled water.

2. Add 1 drop of phenolphthalein indicator solution and titrate with 1N HCℓ to the permanent disappearance of the pink color. The solution should remain colorless for at least 3 minutes at the endpoint. Note: It will be necessary to stir the slurry well in order to dissolve all of the lumps of lime. Addition of 1-2 drops of thymolphthalein will result in a violet to pink color change just prior to the disappearance of the pink phenolphthalein color, which may aid the observation of the endpoint.

3. Calculations:

   (a) Available alkalinity (as millimoles OH^-/g) = $\frac{(\text{mℓ HCℓ})(\underline{\text{N}}\text{ of HCℓ})}{\text{g sample}}$

   (b) Available alkalinity (expressed as

$$\%Ca(OH)_2 = \frac{(\text{mℓ HCℓ})\ (\underline{\text{N}}\ \text{HCℓ})(.0741)}{(\text{g sample})(2)}$$

   where: 0.741 is the millimolecular weight of $Ca(OH)_2$

Method #59 - Total Calcium in Lime

1. Transfer between 0.10 g and 0.12 g (weighed to ± 0.0001 g) of well-mixed sample into an Erlenmeyer flask containing 50 mℓ of distilled water.

2. Add 5 mℓ of 10% HCℓ and stir to dissolve all solids.

3. Continue determination as in Method #55, Step 5, except that the KCN may be omitted.

4. Calculations:

$$\text{Calcium (millimole/g)} = \frac{(\text{mℓ EDTA})(\underline{\text{M}}\text{ of EDTA})}{\text{g sample}}$$

Method #60 - Carbonate in Lime

Use Method #54 (Carbonate in Solids) with a 1.0 to 1.1 g sample, except that Step 5 (addition of H_2O_2) may be omitted. Calculations are the same.

Method #62 - Carbonate in Soda Ash

1. Transfer between 0.11 g and 0.12 g (weighed to 0.0001 g) of well-mixed sample into an Erlenmeyer flask containing 60-70 mℓ of distilled water.

2. Add 1 drop of phenolphthalein indicator solution and titrate with 0.1N HCℓ to the disappearance of the pink color. Call this volume of titrant "A".

3. Add 2-3 drops of bromocresol green indicator solution, and continue the titration with 0.1N HCℓ until a yellow color is reached. Then add 2-3 mℓ more of titrant. Call this volume of titrant (from the phenolphthalein endpoint on) "B".

4. Transfer the titrated solution to a beaker and boil for 10 minutes or so. Cool the solution.

5. Back titrate with 0.1N NaOH to a green endpoint. Call this volume of NaOH "C".

6. Calculations:

Total carbonate in soda ash (as % Na_2CO_3) =

$$\frac{[(B \times \underline{N}\ HC\ell) - (C \times \underline{N}\ NaOH)] \times 0.106}{\text{g sample}} \times 100$$

where: 0.106 is the millimolecular weight of Na_2CO_3

Excess alkalinity in soda ash (as % NaOH) =

$$\frac{\{(A \times \underline{N}\ HC\ell) - [(B \times \underline{N}\ HC\ ) - (C \times \underline{N}\ HaOH)]\}}{\text{g sample}} \times .040 \times 100$$

where: 0.040 is the millimolecular weight of NaOH

APPENDIX D

SYSTEM ECONOMICS

APPENDIX D

SYSTEM ECONOMICS

Based on operating results to date, General Motors has provided Table D-1 which summarizes the costs of constructing and operating the Chevrolet-Parma Double Alkali SO_2 control facility.

Table D-1

SYSTEM ECONOMICS

Total Capital Cost = $3.2 Million (1975$)

Operating Costs/Ton Coal = $11.70[1]

Scrubber Operating Costs (1975$)

Component	$/Ton of Coal[2]	Mils/Kwh[3]
Lime	0.98	0.41
Soda Ash	0.82	0.34
Water	0.16	0.07
Electricity	1.32	0.55
Solid Waste Handling	0.81	0.34
Labor	2.04	0.85
Maintenance	1.05	0.44
Capital Charge	4.55	1.90
Total	11.73	4.90

Total Annual Costs = $643,500

(1) Based upon burning 55,000 TPY coal (i.e., approximately 55% load factor).

(2) Supplied by General Motors.

(3) Based on equivalent heat rate of 10,000 Btu/kwh and firing 12,000 Btu/lb coal.